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XXXIII. *A Piezo-Electric Oscillograph.* By C. E. WYNN-WILLIAMS, M.Sc., *University Research Student, University College of North Wales, Bangor* \*.

[Plate V.]

THE present research was undertaken with the object of ascertaining whether a practical oscillograph could be constructed by utilizing what is known as the converse piezo-electrical effect, and if so, of examining its characteristics.

The converse piezo-electrical phenomenon consists of the mechanical strain produced in a crystal when suitably electrified. This strain may be a linear extension or contraction, as in the case of quartz, or a combined linear and torsional effect as in the case of rochelle salt crystals.

It was thought probable that an oscillograph constructed on this principle would possess certain advantages over some of the types at present in use. In the first place, it would probably have a small capacity, and, being electrostatic, would not interfere to any great extent with the working of the apparatus to which it was connected. As most electrostatic oscillographs at present in use require high voltages to obtain appreciable amplitudes, it was thought that by suitable choice of material an advantage would be gained by being able to operate at a comparatively low voltage. In addition, as the present low-voltage oscillographs are mostly

\* Communicated by Prof. E. Taylor Jones, D.Sc., F.Inst.P.

current operated, and not electrostatic, the advantages of both types would be combined in one instrument. A further possibility lay in the fact that the natural frequency of vibration of a crystal might be high, a desirable feature in all oscillographs.

The piezo-electric substances experimented with in the present research are quartz and rochelle salt. Other substances, however, show this effect, *i. e.* boracite, tourmaline, etc. In a paper by Dr. Nicolson\*, it is stated that most substances which exhibit optical activity also show this phenomenon. He points out that it is probably due to asymmetry in the crystal,—molecular in the case of quartz, boracite, etc., and atomic in the case of organic substances like rochelle salt. He states that up to the time of writing rochelle salt has been found to have the greatest known activity, but it is quite probable that other substances may be discovered possessing a greater sensitivity. Dr. Nicolson also shows that, by special treatment, the sensitivity of rochelle salt may be increased, and that under suitable conditions of growth, crystals are obtained which show a torsional effect not present in the normal crystal.

It was hoped that amongst the substances which show this effect, one or more might be found to be suitable for the purpose of oscillograph construction. In order to see what condition the substance should, however, fulfil, it will be well to examine the theory of the oscillograph in a general way.

### *Theory of the Oscillograph.*

In principle the oscillograph is an instrument which gives a graphical representation of some varying quantity such as an electrical current or potential. This is done by making the electrical quantity control the movement in one direction of a spot of light falling on a photographic plate or film. Either the plate or spot is also moved at some definite rate perpendicularly to this direction, the plane of the plate being at right angles to both of these directions. In this way the light spot describes a curve relatively to the plate, which curve is photographed. From this, provided the characteristics of the instrument are known, the value at any moment of the quantity under consideration can be calculated. If possible it is arranged that the spot moves with uniform velocity along the "*x*" axis of the plate, the "*y*" coordinate

\* A. M. Nicolson, "The Piezo-Electric Effect in the Composite Rochelle Salt Crystal," presented at a joint meeting of the A.I.E.E. and the American Physical Society, Philadelphia, Pa., Oct. 9, 1919.



being a function of the electrical quantity under examination, so that  $x$  is proportional to the time, while  $y$  is usually proportional to the electrical quantity  $E$ , or to its square. If  $y$  is a linear function of the electrical quantity, a scale representation of it results.

The nearest approach to the ideal instrument is the cathode ray oscillograph, in which the mechanical-electrical medium is a beam of cathode rays deflected by an electrostatic or a magnetic field. Here the inertia of the system is negligible. In practically all other oscillographs the position of the spot is determined by a mirror, which, in turn, is controlled by the electrical quantity. This introduces extra inertia, which distorts the curve obtained, and limits the usefulness of the instrument.

If the system has a natural periodicity  $n$ , and specific damping  $k$ , and is not a coupled system, we get for the dynamical equation,

$$\frac{d^2y}{dt^2} + k \frac{dy}{dt} + n^2y = E,$$

where  $E$  represents the applied force per unit of inertia. Here it is assumed that a linear relation exists between the displacement and the applied force, and that  $n$  and  $k$  are constants. Expanding  $E$  by Fourier's theorem we get

$$E = E_0 + \sum_{m=1}^{m=\infty} E_m \epsilon^{-\mu_m t} \left\{ \begin{matrix} \sin \\ \cos \end{matrix} \right\} mpt.$$

Substituting this expression for  $E$  in the differential equation and integrating, we get

$$y = A \epsilon^{-\frac{k}{2}t} \sin \left( \sqrt{n^2 - \frac{k^2}{4}} t + \alpha \right) + \left[ \frac{E_0}{n^2} + \sum \frac{E_m \epsilon^{-\mu t} \left\{ \begin{matrix} \sin \\ \cos \end{matrix} \right\} (mpt - \phi)}{\sqrt{\{n^2 - m^2 p^2 + \mu(\mu - k)\}^2 + m^2 p^2 (2\mu - k)^2}} \right]$$

where  $\tan \phi = \frac{mp(k - 2\mu)}{n^2 - m^2 p^2 + \mu(\mu - k)},$

The first term of the expression (*i. e.* the complementary function) represents the free oscillations of the system in its own period. It will be observed that these die away unless  $k=0$ . If  $k$  is not less than  $2n$ , no free oscillations will be recorded, the system being aperiodic. As it is undesirable

to have the free oscillations recorded, it is arranged that  $k$  shall not be less than  $2n$ . This is the first requirement.

The second part of the solution—the particular integral—represents the forced oscillations of the system produced by the electrical force. Every term in the expression for  $E$  has a corresponding term in the solution, so that all harmonics appear in the record. It will be observed, however, that although the periodicity,  $p$ , and the damping,  $\mu$ , are correctly recorded, the amplitude scale and the phase lag,  $\phi$ , are functions of  $p$ , and are therefore different for the various components of  $E$ , consequently the curve is usually distorted to some extent, and does not give a true representation of the quantity  $E$ .

To examine this distortion, assume that  $E$  is a harmonic function without damping; then the second expression reduces to

$$\frac{E \sin (pt - \phi)}{\sqrt{(n^2 - p^2)^2 + k^2 p^2}},$$

where  $\tan \phi = \frac{kp}{n^2 - p^2}.$

The amplitude scale is given by

$$\frac{E}{\sqrt{(n^2 - p^2)^2 + k^2 p^2}},$$

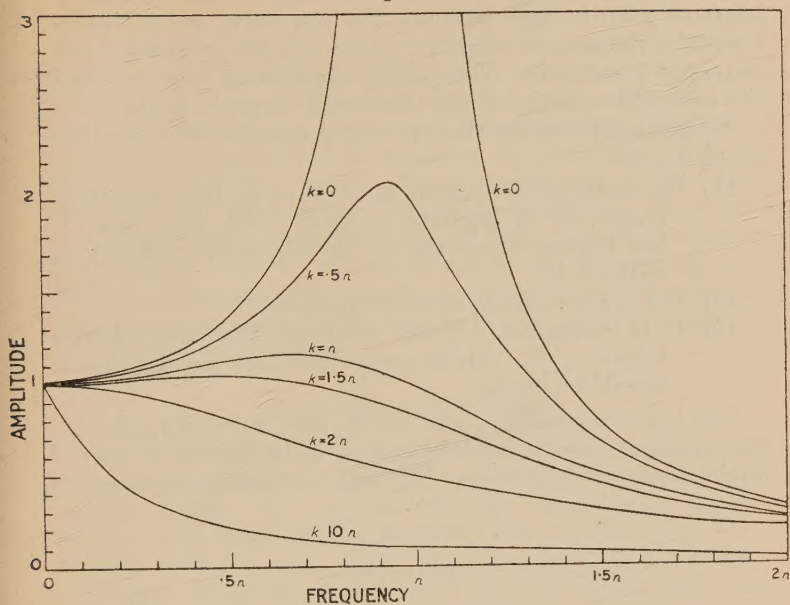
and is shown plotted against  $p$  for various values of  $k$  in fig. 1. When  $k=0$ , we get the ordinary resonance curve, with an infinite amplitude at  $p=n$ . As it is desirable to have all oscillations recorded with the same amplitude scale, the curve for  $k=1.5n$  would seem to be a suitable one, as it is fairly flat for some distance from the origin, but since  $k$  must not be less than  $2n$  to ensure aperiodicity, the instrument will have to be worked on the curve for  $k=2n$ . In this case the amplitude of the oscillations decreases as the frequency increases. Although this may be corrected for, it is usual to keep the working range small, say from  $p=0$  to  $p=0.1n$  or  $0.2n$ , and to ignore the error (*i. e.*, the error introduced by assuming that the amplitude is constant and equal to its value at  $p=0$ ). In the first case this amounts to 0.7 per cent., and in the latter, 4 per cent. for this curve.

Thus, in order to obtain a true record, the natural frequency of the instrument must be from five to ten times greater than the highest frequency to be recorded, when dealing with more than one oscillation. This gives the second condition to be fulfilled.

The variation in phase lag is shown in fig. 2,  $\phi$  being plotted against  $p$  for various values of  $k$ . It will be seen

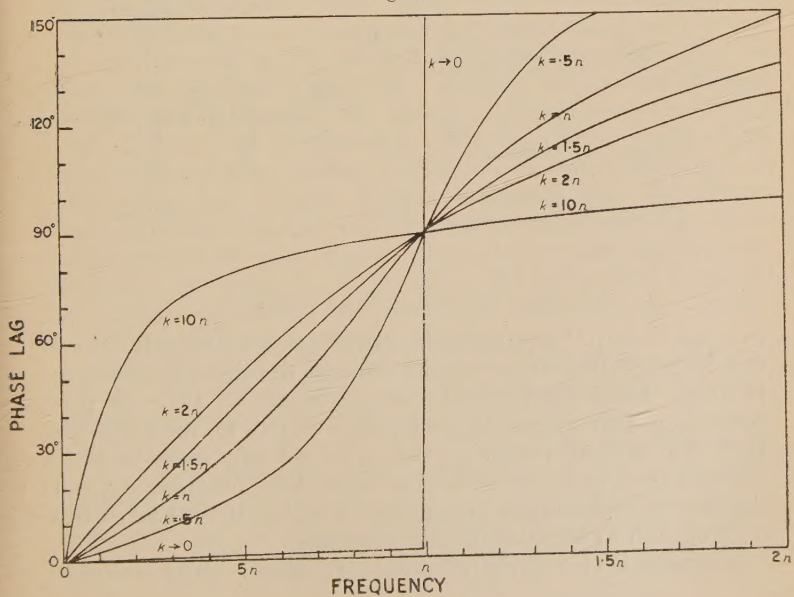


Fig. 1.



Amplitude-frequency Curves.

Fig. 2.



Phase-frequency Curves.

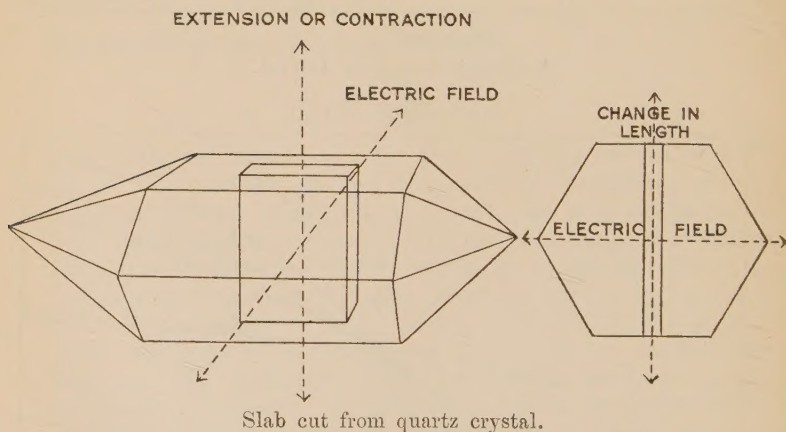
that for  $k=2n$  the curve is fairly straight over the ranges  $p=0$  to  $p=0.1n$  or to  $p=0.2n$ , the respective errors introduced by assuming a constant phase lag being about 3 per cent. and 7 per cent. This again emphasizes the fact that the natural frequency of the instrument must be high.

Summing up, we see that the requirements of an oscillograph are :—

- (1) The mechanical system must have as high a natural frequency as possible, at least 5–10 times that of the highest frequency to be recorded, or distortion will result.
- (2) The system should be made aperiodic.
- (3) It is *convenient*, but not essential, that the relation between the displacement and the applied force should be linear.

The last two conditions are fairly easy to satisfy, but the first presents some difficulty when it is desired to record high frequency oscillations. The highest frequency obtainable

Fig. 3.



in most "strip" oscillographs (such as the Duddell) is of the order of 10,000 per second, so that the limit of working is about 1000–2000 vibrations per second. It is in this connexion that piezo-electricity is resorted to, in the hope that the natural frequency of some of the piezo-electric crystals may be so much higher than that obtainable from the present mechanical systems as to enable the range of the oscillograph to be substantially increased.

Suppose that a strip of quartz is taken. The velocity



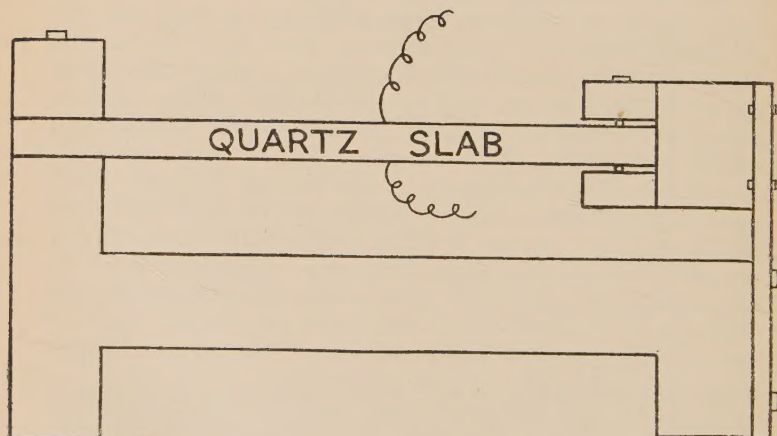
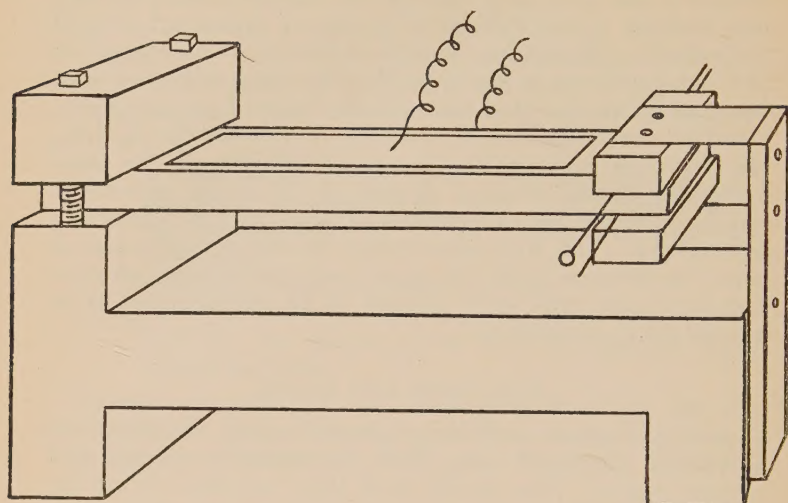
of sound in quartz is about 400,000 cm./second. If the strip is 5 cm. long and has one end clamped, the free end can execute a longitudinal vibration of frequency 20,000 per second. By cutting the slab of quartz from a crystal in the manner shown in fig. 3, so that the long edge is 5 cm. long, and clamping it at one end, the faces of the slab being silvered and connected to a source of alternating E.M.F., the free end will execute forced oscillations of the same frequency as the source. Hence, provided the movement can be recorded, an oscillograph of high natural frequency is obtained. The first experiments in the present research were undertaken with the object of ascertaining whether the movement was large enough to be recorded and so be turned into practical use.

### *Experiments with Quartz.*

A slab of quartz, suitably cut, was obtained, of dimensions 5 cm.  $\times$  2 cm.  $\times$  0.3 cm. This was carefully silvered and copper plated. The copper was then removed round the edges, until only two plates were left on the faces, with about 1 mm. clearance along the sides, and about 5 mm. at the ends. Leads were connected to both plates. One end of the slab was firmly clamped. The other end was covered with thin emery paper to give a frictional surface, and two thin steel needles, 0.7 mm. diameter, were held against the emery paper by two ebonite blocks (also covered with emery paper) fastened to the end of a V-shaped spring. This in turn was clamped to the base. A small mirror was fastened to the end of one of the needles. Fig. 4 shows a section and sketch of the instrument. Any change in length of the quartz would thus produce a rotation of the needles and so tilt the mirror. A spot of light, reflected from the mirror, was carefully watched while the plates were raised to a P.D. of about 10,000 volts (direct), but no movement was observed. This was the highest voltage that could be reached in air, so the whole instrument was immersed in oil and the experiment repeated, with no better results.

It was thought that interference methods might give better results; various methods were experimented with, the most satisfactory being the "Newton's rings" method. A small piece of blackened glass was attached to the free end of the quartz, and a long-focus lens to the base of the instrument, parallel and close to the glass. Rings were seen, using a sodium flame as a source of light. These were observed through a telescope, while the plates were charged to about

Fig. 4.



Quartz Oscillograph.

10,000 volts by means of a small wimshurst machine. It was found that about 10,000 volts (measured by the spark length) would produce a movement of one ring (from "dark" to "dark"). Hence the free end must have moved through a distance equal to half the wave-length of sodium



light, viz.:— $2.948 \times 10^{-5}$  cm. This movement was smaller than was expected, and accounts for the fact that no measurable deflexions were obtained by the mirror method.

It was decided to abandon the quartz (temporarily at least) and to turn to rochelle salt, which is much more sensitive, as an alternative.

In passing, it is interesting to note that audible "clicks" were heard from the quartz on charging and discharging the plates from the 200 volt mains. Assuming a linear voltage-displacement relation, it will be seen that the movement of the free end is only  $5.897 \times 10^{-7}$  cm. Later, on trying the effect of alternating E.M.F.'s of about 150–200 volts (R.M.S.) supplied by a valve, audible notes were produced. This method could evidently be used for the determination of the minimum intensity of sound necessary for audibility.

#### *Rochelle Salt.*

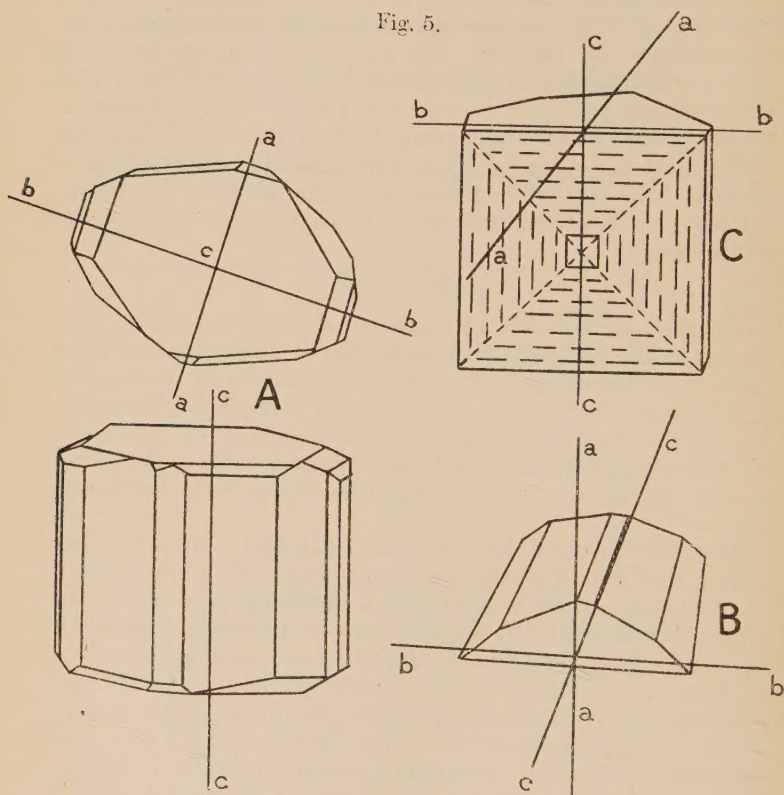
Crystals of rochelle salt are much more sensitive than quartz. The piezo-electric properties of this substance have been made the subject of considerable research during the last three or four years, especially in America. Valasek \* has shown that the substance exhibits a kind of hysteresis similar to magnetic hysteresis, and has succeeded in obtaining a loop for it, of a similar shape to a magnetic hysteresis loop.

Dr. Nicolson, of the Western Electric Company, has shown that with suitable conditions of growth, a crystal may be obtained which will exhibit a torsional piezo-electrical effect. Ordinarily the crystals are of the shape shown in fig. 5 A. Such crystals are formed by growing on a mercury surface, or by being suspended in the solution. If a slice be cut from such a crystal, normal to the (*a*) axis, and having edges making angles of  $45^\circ$  with the (*b*) and (*c*) axes, the slice will exhibit piezo-electrical phenomena similar to quartz. This effect is purely linear. If, however, a crystal is grown on a piece of plate glass or mercury surface, with the (*a*) axis vertical, a sort of "flat" crystal is obtained. (See fig. 5 B. Figs. 5 A and 5 B are reproduced from Nicolson's paper.) Crystals so grown, especially those grown by cooling a saturated solution, show a peculiar marking, termed an "hour-glass" marking. The small crystal used as a nucleus lies in the centre of the flat face, and as the crystal gradually grows, different layers become strained, giving the peculiar

\* Valasek, "Piezo-Electric and Allied Phenomena in Rochelle Salt," Phys. Rev. April 1921.

appearance \* shown in fig. 5 c. It will be observed that the crystal appears to contain two pyramids, having their apices on the nucleus, and their bases at the ends of the crystal. If these two pyramids are connected to one terminal of the voltage supply, and a connexion from the other terminal is made to the rest of the crystal, so that both

Fig. 5.



Rochelle Salt Crystals.

pyramids are charged with respect to it, an internal torsional stress is set up, which results in the top pyramid being twisted relatively to the bottom one about the (c) axis. The magnitude of this twist depends upon the particular crystal, and may be large or small, regardless of size of the crystal, dryness having much influence. In Nicolson's paper it is mentioned that soaking the crystal in alcohol for some hours

\* Such crystals are termed "composite."



before drying increases this effect, and that only crystals showing the hour-glass marking give rise to large values. He states that in one case (a crystal 7 cm. long) a twist of  $10^{-5}$  radian per volt was obtained.

In practice, connexion is made to the crystal by two tin-foil electrodes fastened to the ends (by wax or shellac varnish) and by a third "girdle" of foil round the middle of the crystal. The width of this latter is usually about one-half to three-quarters the length of the crystal. The two ends, connected together, form one pole, and the girdle the other. Wood's alloy has also been used for the end electrodes.

Evidently the electrical conditions within the crystal are much more complex than within a "plate." As far as can be ascertained, the theory has not yet been worked out for this type of strain.

A torsional strain being much more easily magnified, it was decided that this type of crystal might be used more successfully for oscillograph purposes than quartz, as it has also the advantage of being more sensitive, and therefore of requiring a lower working voltage.

### *Growth of Rochelle Salt Crystals.*

Several experimenters engaged in research on this substance, and also some chemical firms, were communicated with to see if the finished crystals could be obtained, but unfortunately none were available\*. Accordingly much time had to be spent in growing suitable specimens.

The only available information on this subject was obtained from Nicolson's paper. As, however, only a general outline is given by him, and no details are furnished, a number of different conditions of growth had to be tried.

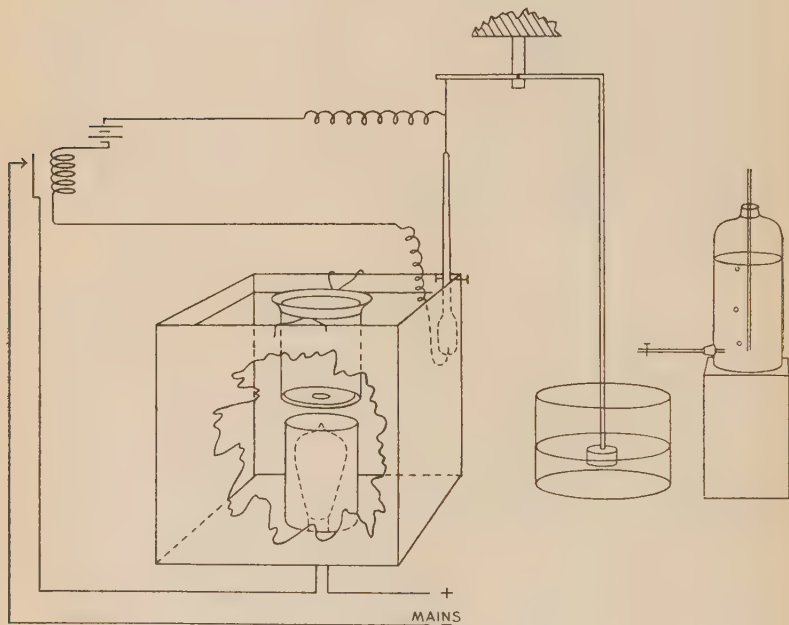
In the first experiments, growth was attempted by the slow evaporation of a solution of the salt, at room temperature. Small fairly well shaped crystals were obtained in this manner, but they were perfectly clear, and did not show the composite structure mentioned, which appears to be necessary for the torsional effect. The effect of hastening the rate of evaporation was tried by placing the containing vessel on a board over a gas radiator. This resulted in the crystals forming more quickly, but trouble was caused by small crystals formed at the surface of the liquid falling on

\* Since the above was written, a large specimen has very kindly been presented by the International Western Electric Co., to whom the writer's thanks are due. So far, no opportunity has been found for testing it, but in appearance it resembles those obtained by the writer.

top of the "seed" crystals at the bottom of the vessel, and so disturbing the growth.

Experiments were then conducted to see if crystals could be obtained more readily by cooling a saturated solution. A saturated solution contained in a beaker was placed in a larger vessel full of water at the same temperature (about  $30^{\circ}\text{C}.$ ). This latter vessel was jacketted with cotton-wool. A small seed crystal was introduced into the saturated solution, and the whole left to cool overnight. This method resulted in a crop of small irregular crystals—evidently due

Fig. 6.



Thermostat and Control.

to too rapid a fall of temperature. This was repeated with the whole apparatus placed over a radiator, whose temperature was slowly lowered by periodically turning the gas lower. The resulting crystals were a little better, but not satisfactory; evidently uneven heating was one source of trouble.

A method which gave good results was found by constructing a thermostat whose temperature could be automatically lowered at any desired rate. Fig. 6 illustrates the arrangement. The water-bath consisted of a cubical tin



box of about 9 in. side. Into the bottom of this a cylinder was let, open from the outside, in which an electric lamp could be placed to supply the necessary heat. A 60 watt lamp was found to be ample to keep the bath at  $50^{\circ}\text{C}$ . The box was jacketted with cotton-wool. A thermometer was constructed from fairly wide capillary tubing, with a platinum contact fused into the bulb. This was placed in the bath. A wire passed down the bore of the tube to make contact with the mercury thread at any desired temperature. When contact was made, a local low voltage circuit was closed, which resulted in the lamp being extinguished by means of a reversed relay. The thermometer contact was sensitive to about 0.3 of a degree. In order to lower the temperature automatically, the upper end of the wire was attached by means of a lever to a float in a vessel of water. Water dropping from a capillary tube connected with a constant-pressure bottle slowly raised the float and so pushed the wire down the thermometer. By this means, the temperature could be lowered as slowly as 0.5 degree per hour.

The actual growth took place in a beaker of about 700 c.c. capacity suspended in the bath. As these crystals require to be grown on a flat surface, a layer of mercury was placed at the bottom of the beaker. It was found, however, that as the crystal increased in mass it sank a little further into the mercury, and so developed a slightly convex surface. This was rectified by growing the crystals on a piece of plate glass floating on the mercury. This ensured that the surface was both level and flat.

Seed crystals were obtained by cooling rapidly, and from the crop of small crystals so obtained, suitable ones were picked out.

The solution must be carefully filtered, otherwise dust, etc., form nuclei for crystals. The best method of carrying out this method was found to be as follows. The saturation temperature of the solution was determined previously, and the thermostat brought to about 3 or 4 degrees above this temperature. The solution was heated to the temperature of the thermostat, and the seed crystal warmed to this temperature by being placed for a few minutes in a dry test-tube immersed in the solution. Unless this was done, the crystal cracked on being dropped into the solution, on account of the sudden expansion of the outer layers. The beaker containing the solution was then suspended in the thermostat, the glass plate and mercury dropped in, and, finally, the seed crystal was introduced and moved to a suitable position near the centre of the plate. It was found

necessary to suspend a sort of "umbrella" consisting of a circular glass plate, slightly less in diameter than the beaker, just below the liquid surface. This prevented crystals formed at the liquid surface from falling on the growing crystal and hindering perfect formation.

It was found best not to cool continually, but to lower the temperature slowly (about  $1^{\circ}$  per hour) to about 2 or 3 degrees below saturation temperature, and to keep the solution at this temperature for some time. With care, crystals as large as 6 cm.  $\times$  5 cm. were grown by this method.

The actual time of growth varied with the size of the crystal. A crystal 2 cm.  $\times$  2 cm. could be grown in about 8 hours. It was found difficult to prevent the larger crystals from developing flaws due to side growths.

Another method that gave good crystals was to allow a solution to cool in a small hot-air oven. This consisted of a cubical copper oven, about 1 ft. side, covered with cotton-wool, and heated by means of a 20 watt electric lamp placed inside. Provided it was left undisturbed, in a room free from draughts, the temperature was found to keep constant to within about  $1^{\circ}$  C. for long periods,—about 12 hours or more,—without the use of a regulator.

A solution, saturated at about 3 or 4 degrees above the oven temperature, was heated to about 8 degrees above that temperature, and the seed crystal introduced as before, together with the plate, mercury, etc. The whole was then left in the oven for about 12 hours. Crystals up to about 4 cm. square were obtained by this method.

The latter method seemed to yield the better formed specimens, and it was more free from trouble due to small crystals interfering with the growth than any of the other methods tried. Probably the solution was kept at a more uniform temperature throughout than it was in the thermostat method, in which no stirring apparatus was provided.

Crystals of all sizes from about 1.5 cm. square to about 6 cm. were grown and tried. It was exceedingly difficult to prevent the large crystals from developing flaws and cracks. They often cracked, on being removed from the solution, in coming into contact with cold air, even the temperature of the finger being sufficient in some cases. On the whole, crystals 2–4 cm. square were the largest which could be grown satisfactorily.

#### *Preparation of the Crystals for Experimental Work.*

According to Nicolson, if the crystals are soaked for some hours in alcohol, and dried, they are rendered more sensitive

for the direct piezo-electric effect. This has been found to be the case for the converse effect also, and for oscillograph work an additional advantage arises from the fact that crystals so treated appear to stand the voltage better than the raw crystal. So far, it has not been ascertained whether the treatment affects the natural frequency and damping of the crystal, but it is quite possible that these properties are affected by the degree of dryness of the crystal.

While Nicolson finds desiccation of the crystal to be an advantage, Valasek shows that the linear piezo-electric effect is decreased by drying. It should be mentioned, however, that Valasek carried his drying process to a higher stage than Nicolson by using phosphorus pentoxide. This may possibly account for the different results obtained by the two experimenters.

On the whole, for the purpose of the present research, it has been found advisable to soak the crystal in alcohol, even if only on account of the increase in dielectric strength.

The crystal is taken from the solution and immediately placed in a vessel full of alcohol, at the same temperature as the solution. It is at this stage that cracks usually appear, and care must be taken not to let the crystal experience any sudden change of temperature. It is left in the alcohol for about 12 hours, preferably in a warm place, and then a fresh supply is poured on for a further six hours. This treatment changes the appearance of the crystal somewhat, the clearness disappearing and being replaced by a translucence. After the soaking has been completed, the crystal is removed and placed in a drying oven, kept at a temperature of from  $35^{\circ}$  to  $40^{\circ}$  C., for several days—the longer the better.  $40^{\circ}$  should not be exceeded as the crystals lose their sensitiveness if heated too strongly.

The electrodes consist of pieces of tinfoil cut to appropriate shapes, tags being left on for connexion. Low melting wax (below  $40^{\circ}$ ) or shellac varnish may be used to attach them to the crystal. The latter is the more satisfactory, but the crystal must be re-dried after application. The width of the girdle should be about one-half the length of the crystal, and the electrodes should be well pressed into position, a thin coating of shellac varnish having been applied previously. Celluloid dissolved in amyl acetate has also been used for this purpose; it has the advantage of setting more quickly than shellac. Wood's metal is not recommended for two reasons. In the first place,  $55^{\circ}$  C., its melting point, is rather too high a temperature to which to subject the crystal, and also, the large masses at the ends would tend to lower

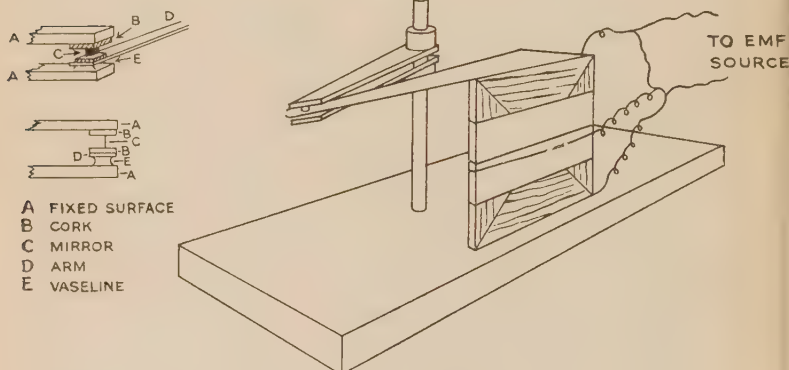


the natural frequency. The melting point can be lowered by the addition of mercury, but on the whole this material is not satisfactory. Filing the ends of the crystal concave, as recommended by Nicolson, was not found to cause any improvement. Very often this process causes flaws to appear. The crystals were used in the form which they had when taken out of the solution, and were found to possess sufficient sensitiveness in this form after treatment with alcohol.

### *Preliminary Measurements.*

Measurements made with a crystal 2.5 cm. square by 1 cm. thick showed that the torsion was proportional to the voltage, and for 200 volts was about  $10^{-4}$  radian. A dissymmetry for + and - potentials was also observed, the deflexions being greater in one direction.

Fig. 7.



Rochelle Salt Oscillograph.

In order to obtain sufficient magnification, a light but rigid arm of sheet aluminium, folded so as to have a girder section, was attached to the top of the crystal, extending horizontally to 2 or 3 cm. from the centre of the crystal. Between this arm and a fixed surface placed just above it was held a small plane mirror, about 1 square mm. in area. The plane of the mirror was parallel to the plane face of the crystal. When too thin and clamped in this way, the mirror was liable to be bent slightly convex or concave, making sharp focussing of the spot impossible. Accordingly thicker mirrors had to be used. In order to prevent slipping, the tip of the arm and the fixed surface were covered with thin slips of cork. This arrangement was found to be very satisfactory, amplitudes of 1.5 cm. on either side of zero being at times obtainable, using an image distance of 1 metre. Fig. 7 shows the arrangement.

The actual arrangement of the apparatus for recording the curves is as follows:—The whole is set up in a darkened room. A small pinhole, having the crater of an arc lamp focussed on it, is used as a source of light. From this, a beam falls on the oscillograph mirror, and (if required) on to a mirror attached to the prong of a tuning-fork placed near the oscillograph. This gives a time scale if the frequency of the fork is known. These mirrors are so arranged that on tilting they deflect the beam in a vertical plane. After reflexion from the small mirrors, the beams fall on a concave mirror, of about 50 cm. radius of curvature, attached to a horizontal turntable, rotated at any desired speed by an electric motor.

It is desirable (for reasons to be given later) that the crystal should not be subjected to the E.M.F. longer than is necessary, so a cam was arranged on the turntable which opened and closed a two-way mercury switch, at the moment when the spot of light passed the plate. Normally, the crystal was shortcircuited by one contact. At the correct moment this was broken, and contact was established with the live cup. This was also found useful for "make" and "break" photographs, etc. A safety resistance was placed in the circuit, consisting of a 200-volt metal filament lamp, to prevent inconvenience due to shortcircuit. (The impedance of the crystal was large compared with the resistance of the lamp.)

In order to determine whether the crystal was suitable for oscillograph work, investigations were conducted to determine whether the necessary conditions were satisfied. In the first place it is necessary to know what relation exists between the applied E.M.F. and the corresponding displacement. Rough measurements had already been made as to the deflexions at various voltages, and as far as could be judged, a linear relation seemed to exist. It must be observed, however, that equal + and — voltages do not necessarily or generally give equal + and — deflexions,—*i. e.*, the voltage-deflexion curve is not the same on opposite sides of zero. The effect of this on an oscillogram is to make one side of the curve appear to have a greater amplitude than the other—a sort of rectification effect such as is obtained in wireless by working at the lower bend of a valve characteristic. This is not serious unless the change of the voltage-deflexion curve is very pronounced. As a rule, it may be neglected, as there is practically no distortion. It is possible, however, to overcome the difficulty in quite a simple manner, by subjecting the crystal to a steady voltage equal to the peak

voltage to be dealt with. By this means, the peak voltage ( $E$ ) is superimposed on the steady voltage ( $E$ ), and we get an alternation from 0 to  $+(E + E)$  or 0 to  $-(E + E)$  instead of from  $-E$  to  $+E$ , the oscillograph thereby being worked only on one side of zero. This has the objection of raising the new peak voltage to double its previous value, and so rendering the crystal more liable to break down. Usually, however, as explained, the dissymmetry may be ignored.

The rough measurements as to the linear relation were verified by photographing the sine wave of an alternator running at a constant speed (50 cycles/sec.) for different values of R.M.S. voltage, from 0 to 260. The amplitudes of these curves were measured, and a graph drawn showing the relation between the amplitude and the voltage. It was found that, as nearly as could be measured, the graph was linear. Hence, the linear relation may be said to be reasonably satisfied. Most probably the relation holds to a higher degree of accuracy than the measurements made by this method show, but in any case it is sufficiently accurate for the present purpose.

#### *Natural Frequency and Damping.*

In order to investigate the natural frequency and damping of the crystal, the automatic switch was arranged so that the crystal was suddenly connected with a source of direct E.M.F. (200 or 400 volts), a photograph being taken at the moment of connexion. If the system is not aperiodic, the sudden shock will set it oscillating in its own period, and damped natural oscillations will appear in the photograph. If, on the other hand,  $k$  is not less than  $2n$ , the resulting photograph will show no trace of free oscillations.

It was found that the oscillograms varied considerably for different crystals. Some were found to show no trace of free oscillations pointing to high damping, while marked oscillations appeared in others. The curve in fig. 8 (Pl. V.), for example, shows a very well marked oscillation after the sudden application of a potential of 440 volts to the crystal. At first, however, when the crystal was freshly formed, no such oscillations were found in the photograph, and the conclusion then drawn was that all crystals were highly damped. Consequently it was thought that the only way of determining the natural frequency was by some resonance method, and attempts were made to obtain a resonance curve for the crystal.

Alternating E.M.F.'s of frequencies from 150 to about



10,000 were produced by means of a transmitting valve, whose grid and plate circuits were coupled by means of large air-core inductances having variable condensers in parallel with one or both for controlling the frequency. R.M.S. voltages of from 70 to 300, as measured by an electrostatic voltmeter, were obtained in this way. Lower frequencies down to 50 were obtained from A.C. generators running at various speeds. These voltages of various frequencies were applied to the crystal, the corresponding curves photographed, and their amplitudes measured. By dividing the amplitude obtained by the voltage for the particular curve, a measure of the amplitude scale for the frequency employed was obtained, and a graph was plotted showing its variation with the frequency. Great trouble was experienced in these experiments owing to the breakdown of the crystals (referred to later) which frequently required a fresh start to be made with new ones, and for this reason no complete curve was obtained at this stage. Evidence was obtained, however, of the existence of a resonance peak usually at a frequency of about 3000, and of a minimum between the peak and zero. From this it will be seen that the system cannot be a simple one as is assumed in the theory, for the curves shown in fig. 1 were plotted on this assumption, and in no case does such a minimum appear. No definite reasons for this behaviour have yet been found. Later attempts at obtaining a resonance curve met with more success, but the results obtained are not complete enough for publication at present.

Some possible explanations of the peculiar form of the resonance curve are, however, suggested, viz. :—

1. The internal damping may be a function of the frequency.

2. The hysteresis effect observed by Valasek may play some part in the matter.

3. The electrical properties of the crystal may vary with the frequency (*e.g.*, the S.I.C. becomes large at resonant frequency, and then swings round to a negative value, as observed by J. G. Frayne)\*.

These suggestions have not yet been fully inquired into, and further work in this direction might lead to interesting results.

The photographs showing free oscillations were not obtained with crystals less than a few months old. It was observed that they were only given by crystals which had been standing idle for a long time. Fresh ones invariably

\* J. G. Frayne, "Reversible Inductivity of Rochelle Salt Crystals," *Phys. Rev.* March 1923.

gave no trace of oscillations. Consequently it must be assumed that some sort of seasoning process such as setting or drying had occurred in the meantime, which altered the quality of the crystal. As far as could be judged by the eye however, the crystals had the same appearance whether of the former or latter type.

The older crystals were found to be much stronger electrically than the fresh ones, although not quite so sensitive. Comparing the two types, it may be stated that when freshly made, crystals are obtained which

1. Behave as if they were strongly damped,
2. Are very sensitive, usually showing suitable deflexions at voltages below 250,
3. Are easily spoiled by electrical breakdown,

and that these crystals, on being left alone, tend to pass to a type in which they are

1. Not strongly damped (not aperiodic),
2. Not so sensitive, usually requiring voltages above 250 for successful operation,
3. Fairly strong electrically,

The advantages of both types are obvious: in practice, the latter type is found to be the more suitable to work with, on account of its comparative freedom from breakdown, but artificial damping has to be applied to render the system aperiodic, and higher voltages must be used. It is quite possible that the crystals pass through a stage in the seasoning process when the damping is just sufficient to make the system aperiodic. If it were possible to keep them in this state, the crystal would be suitable for an oscillograph without artificial damping.

In the case of seasoned crystals, artificial damping is necessary, and the following very simple method was found to be the best way of applying it. A fixed surface is placed beneath and parallel to the metal arm attached to the crystal, and in the narrow space between them a small quantity of vaseline is introduced. By altering the width of the space the thickness of the vaseline film, and so the viscous drag or damping, may be varied (see fig. 7). By careful adjustment the system can be rendered just aperiodic. This method has the advantage of not requiring the moving system to be immersed in oil as is the case in some oscillographs.

Figs. 8 and 9 (Pl. V.) show shock oscillograms for the system undamped and aperiodic respectively. In this particular case the natural frequency was found to be 3190.

Shock curves for the earlier type of crystals obtained resembled fig. 9, showing the presence of some form of internal damping.

It should be noted that the displacement is not instantaneous, although the change of potential is practically so. This may be due to the hysteresis observed by Valasek. The lag varies with different crystals, and the error introduced is not very great as a rule.

In the artificially damped form, we have an oscillograph which is capable of recording voltage oscillations whose working range is from 0 to about 1000 volts. The upper limit is, of course, determined by the strength of the crystal. Higher values than 1000 have been successfully recorded, but the risk of breakdown increases with the voltage.

The frequency range will depend upon the purpose for which the instrument is required. When dealing with a single harmonic applied force, damped or undamped, any frequency *less* than the natural one may be used, provided the amplitude scale for that frequency is known. If two or more components are present however, or if there are harmonics, the frequency of the most rapid vibration to be dealt with should not exceed 0.2 of the natural frequency unless corrections are applied to the curve. Bearing in mind that the natural frequency is usually about 3000, this means that the range will be from 0 to about 600 for compound oscillations, and higher for single oscillations. The instrument would therefore be useful for A.C. engineering, where the fundamental usually lies in the neighbourhood of 50 cycles per second.

The capacity of the average crystal is stated by Nicolson to be from  $10^{-9}$  to  $10^{-8}$  farad, and the A.C. impedance about 200,000 ohms for acoustical frequencies. These values have not yet been verified for the crystals grown by the writer.

The direct current resistance is found to be different according as the girdle is + or -. For a crystal 3 cm. square, the resistances were respectively 4 and 10 megohms, while for a crystal 4 cm. square they were 6.25 and 25 megohms. This dissymmetry was also observed by Nicolson, but he makes no mention of the different values of the deflexion obtained for equal + and - potentials. There is probably some connexion between the two effects.

Bearing in mind the low capacity, and high impedance and resistance, we may regard the instrument as practically electrostatic, and it may be assumed that it will not disturb to any appreciable extent the circuit to which it is connected,



especially when the work consists of the analysis of the voltage curves of A.C. machinery.

It is found that if a crystal be subjected for some time to a moderate alternating voltage of a frequency too near the resonant frequency, its impedance will suddenly diminish, and the crystal will allow an appreciable current to pass. If the voltage be maintained, the current may become sufficiently great to heat the crystal and fuse it up, and probably electrolyse it.

When a crystal reaches this stage (referred to before as the breakdown) its sensitiveness is lost, as no amplitude is obtainable. On being left alone for a time, it recovers its sensitiveness, partly or wholly, depending upon the length of time which has elapsed, but it is afterwards much more liable to breakdown than before. The photographs shown were obtained with a crystal that had recovered after about two months. It was for the purpose of protecting the crystals against breakdown, by subjecting them to the voltage for only a very short time, that the automatic switch was used.

Just before breakdown, the sensitiveness increases enormously for a second or two, a loud sound of the same frequency as the E.M.F. being emitted, and then the amplitude falls to zero as the impedance falls. If the spot of light on the screen be watched while this takes place, it is observed that the oscillations are on one side of the zero position. As the crystal approaches breaking-down point, the mean position travels further from the zero while the amplitude increases, until, finally, the crystal breaks down, and the amplitude falls to zero. If the concave mirror be revolving slowly, a curve similar to the "grid leak" rectification curve of wireless is observed on the screen, but, unfortunately, it has not been found possible, for obvious reasons, to photograph this phenomenon.

Provided the resistance in the circuit is sufficient to prevent the crystal from fusing after breakdown, it is found that there is practically no difference in appearance between it and a good crystal; no cracks or flaws are visible that were not there originally. No explanation can be given of this, but it is possible that some internal disruption takes place. J. H. Morecroft observed a similar effect in the case of a quartz slab, viz.: complete disruption at the resonant frequency with a voltage below the one required to break down the dielectric under normal conditions.

As in the case of quartz, a sound is emitted when a rochelle salt crystal is subjected to an alternating voltage.

This is particularly evident at frequencies of several thousands, and notes can be heard up to the limit of human audibility with a suitable valve oscillator. Such frequencies, however, are liable to break down the crystal. The sound is much louder than in the case of quartz.

### *Examples of Curves obtained.*

The photographs shown in figs. 8 to 15 (Pl. V.) were taken with the object of illustrating the usefulness of the instrument. In all cases the fork frequency was 384.

Figs. 8 and 9, as already explained, are shock oscillograms for a crystal undamped and with artificial damping respectively. These were obtained by changing the potential applied to the crystal suddenly from 0 to 440 volts. If fig. 9 be carefully examined, it will be seen that there is a slight trace of free oscillation recorded at the commencement of the displacement, showing that the damping was just on the point of being sufficient to ensure aperiodicity. The fact that the displacement was not quite instantaneous should also be observed. This has been referred to before.

Fig. 10 shows the curve given by one phase of a 3-phase rotary converter. The R.M.S. voltage was 260. It will be observed that the curve is remarkably free from harmonics—practically a pure sine wave. The frequency, as calculated from the fork scale, which unfortunately is of rather small amplitude in this particular photograph, is 46·9. This curve was given on open circuit, the crystal being simply connected to the two terminals of the machine.

The curve of an inductor alternator (single phase) is given in fig. 11. Owing to the low voltage of the machine (110) a 2-1 step-up transformer was used to raise the voltage before applying it to the crystal. This would, of course, tend to reduce the amplitude of the harmonics. Even so, it will be observed that they are very prominent. The voltage applied to the crystal was 210 R.M.S., and the frequency 109·7.

Fig. 12 gives the open circuit voltage of a high frequency alternator, also of the inductor type, but of different construction to the previous one, intended for wireless work. Here again, the harmonics are in evidence, although the general shape of the curve is different from the previous one. No transformer was used in this case. The R.M.S. voltage was 240 and the frequency 768·0. Comparing these three alternator curves, it will be observed that as the frequency increases, the amplitude scale decreases, as is the case when working on the " $k=2n$ " curve. The third curve,

fig. 12, was beyond the accurate working range of the instrument for compound curves, assuming the range to be from 0 to about 600, but it serves to show what harmonics are present, although they may not be represented in correct proportion.

A valve oscillation is shown in fig. 13. The plate and grid coils were kept shortcircuited by the switch, until this was opened by the mirror turntable. Oscillations were then built up from zero as shown in the photograph. The voltage when the oscillations were steady was 240 R.M.S. Two valves were used in parallel, and the crystal was connected to the terminals of the tuning condenser. The frequency as calculated from the fork scale is 485.0.

Fig. 14 shows a damped oscillation obtained (as in the primary of an induction coil) by unshortcircuiting a condenser connected in series with an inductance and a battery. The crystal was connected to the terminals of the condenser. The capacity being known, the inductance can be calculated. In this case, the capacity was 0.55 mfd.; the frequency recorded was 964.0, and the damping factor, calculated from the curve, 179.9. From these, after correcting for the damping, the inductance works out to be 0.04913 henry. This arrangement thus furnishes a convenient means of determining self-inductances.

Coupled system oscillations are shown in fig. 15. Here, two similar air-core coils were placed near each other, and tuned by condensers to approximately the same frequency. Oscillations were then set up in one circuit by the same method as for the previous curve, and the variation in the primary voltage recorded. By connecting a second oscillograph to the secondary circuit, and arranging the second spot vertically above the first, it was possible to show the transference of energy from one circuit to another.

It is also possible to use this instrument for the study of sound waves, by connecting a microphone and step-up transformer to the grid circuit of a valve, and connecting the plate of the valve, via another transformer, to the crystal. By this means, curves (not reproduced) have been obtained for organ-pipes, etc. Alternating voltages of about 200 are easily obtained at the terminals of the transformer connected to the crystal by whistling into the microphone.

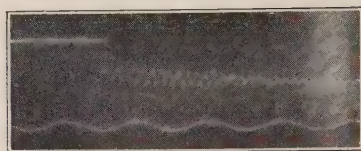
### *Conclusion.*

From the foregoing results and photographs, it is evident that a piezo-electric oscillograph can be constructed with a



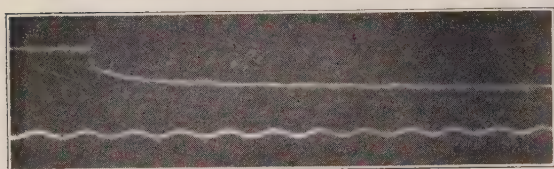


FIG. 8.



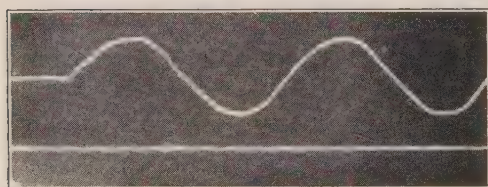
Sudden application of potential--no damping.

FIG. 9.



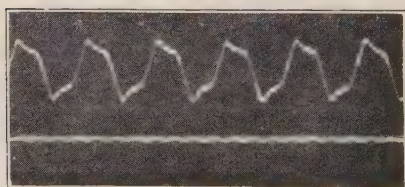
Sudden application of potential—artificial damping.

FIG. 10.



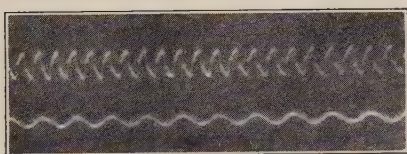
Terminal voltage of rotary converter. 50~, 260 volts.

FIG. 11.



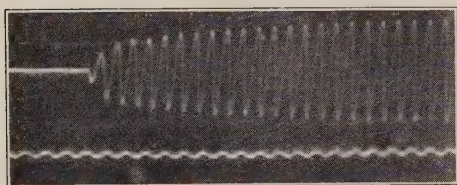
Secondary voltage of transformer, supplied by  
inductor alternator. 100~, 210 volts.

FIG. 12.



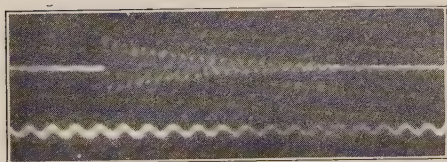
Terminal voltage of high-frequency alternator.  
700~, 240 volts.

FIG. 13.



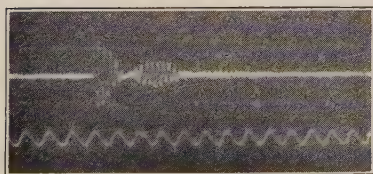
Valve oscillation, frequency 485.

FIG. 14.



Oscillatory discharge of condenser.

FIG. 15.



Oscillatory discharge of condenser in a coupled circuit.





rochelle salt crystal. Such an instrument possesses the following favourable properties:—

1. High voltages are not required for operation as is the case in some electrostatic oscillographs.
2. The moving system does not require oil immersion.
3. Owing to its high resistance and impedance, the instrument is practically electrostatic.
4. The instrument has very low capacity.
5. The adjustment is not difficult.
6. The instrument is compact, of simple construction, and of low cost.

A disadvantage is that rochelle salt crystals do not appear to have very high natural frequencies of vibration, the average value for crystals 3 to 4 cm. square being about 3000. The use of the instrument is thus limited to low frequency work, for which it is, however, very suitable, as indicated by the curves described above.

Possibly some other crystal may be found to be more suitable. If sufficient magnification could be obtained, a quartz oscillograph would probably, owing to the very definite physical properties of this substance, be superior to one of rochelle salt.

The present investigation should be regarded as a preliminary study of a new type of instrument, and as indicating its possibilities, rather than as an exhaustive inquiry into the subject. The work in connexion with it was carried out in the Physical Laboratories of the University College of North Wales, Bangor, and the writer desires to thank Dr. Taylor Jones for his valuable assistance and encouragement during the whole of the work.

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XXXIV. *Some New Methods for the Measurement of Thermal Conductivity.* By T. BARRATT, D.Sc., and R. M. WINTER, M.Sc., *Research Department, Royal Arsenal, Woolwich* \*.

I.

IN a paper on "Thermal and Electrical Conductivities of some of the rarer Metals and Alloys" it was shown by one of us † that the thermal conductivity  $k$  of a thin rod could be expressed by the formula

$$k = \frac{H^2}{pqhV^2} \coth^2 \alpha l,$$

\* Communicated by the Authors. This paper is published by permission of the Director of Artillery.

† T. Barratt, *Proc. Phys. Soc.* xxvi. (5), pp. 347-371 (1914).

where the symbols have the meanings given in Section III. When  $l$  is great, the formula reduces to the very simple expression

$$h = \frac{H^2}{\rho q h V^2}$$

Apart from the simplicity of the formula, the arrangement adopted had the advantage of a "null method" for the measurement of  $H$ , and could be used for a very small sample of wire in the case of a rare metal or alloy. The same formula and arrangement of apparatus were also successfully employed for such bad conductors as glass, various woods, ebonite, and firebrick.

## II. *Measurement of the Emissivity "h."*

The most troublesome and uncertain part of the necessary measurements employed in the use of the formulæ given above is that of  $h$ , the emissivity of the rod or wire. The value of  $h$  depends on the temperature of the enclosure, increasing from 0.000533 at 17°C. to 0.000634 at 100°C. for wires of 1 mm. diameter used by the author\*. It also varies appreciably if the rod is raised more than about 10°C. above the temperature of the enclosure. Prof. C. H. Lees†, in the case of rod 5.85 mm. in diameter, obtained the values 0.000126, 0.000160, and 0.000200 at temperatures -155°, -64°, and 23° C. respectively; while one of us‡, for a rod of about the same dimensions, found an increase from 0.000224 at 18° C. to 0.000265 at 100° C. Lees points out that none of the formulæ suggested up to the present (1908) to express the variation of  $h$  with the temperature  $t$  fitted his results. He himself gave the relation  $h = 1 - bt^{3.2}$  (where  $b$  is a constant) for the case of a small rod at very low temperature in an enclosure only a few, say 10, degrees cooler than itself.

There seems to be little doubt, however, that the value of  $h$  depends on other factors besides the temperature. For example, the dimensions and shape of the heated body and those of the enclosure, as well as the temperature excess of the heated rod, will certainly have an effect, probably considerable, on the value of  $h$ . The emissivity of a thin rod or wire heated in air has been shown to depend chiefly upon convection§. The relative proportions of radiation (including

\* T. Barratt, Proc. Phys. Soc. xxvi. (5); pp. 347-371 (1914).

† C. H. Lees, Phil. Trans. A, ccviii. p. 205 (1908).

‡ T. Barratt, Proc. Phys. Soc. xxvii. pp. 81-93 (1914).

§ T. Barratt, Proc. Phys. Soc. xxviii. pp. 1-13 (1915).

conduction) and convection vary considerably, however, with the diameter of the rod or wire and with the nature of its surface. For example, in the case of a metal wire of 1 mm. in diameter it was shown that of 100 parts of "total heat" lost from the wire at  $12^{\circ}\text{C}$ ., only 2.5 consist of radiation for a bare wire and 12.6 for a blackened wire, the remainder being due to natural or free convection. At  $100^{\circ}\text{C}$ . these percentages become 4.4 and 20.7 respectively, the wire in each case being heated not more than  $10^{\circ}\text{C}$ . above the temperature of the enclosure in which it was placed. For a cylinder of about 5 mm. diameter, the percentage of radiation was found to be 10 for the bare surface and 37 for the blackened surface\*.

In the experiments referred to in Section I.,  $h$  had to be measured in a separate experiment under conditions as nearly as possible similar to those employed in the main experiment. The assumption was made that the value of  $h$  was the same in both cases. If it was required to measure  $k$  at different temperatures, it was necessary to measure  $h$  separately for each temperature.

It would be preferable, therefore, to eliminate  $h$  entirely from the formulæ; and it is proposed in this paper to develop expressions for the thermal conductivity  $k$  which do not involve a separate measurement of  $h$ †. This will be done first as a general proposition, the formula being applicable to any material, and avoiding certain approximations made in the paper referred to in Section I. Thereafter certain particular cases will be considered which are of experimental interest. An expression for the calculation of  $h$  itself will also be given. (See Section III., 6.)

### III. *Expressions for the Thermal Conductivity "k."*

The propositions to be dealt with are as follows:—

- (1) To find the thermal conductivity  $k$  from measurements of the dimensions of the rod, the amount of heat supplied per second, the temperature of the hot end, and the temperature of one other point on the rod.
- (2) A particular case of (1), applicable only when the rod is long.

\* T. Barratt and A. J. Scott, Proc. Phys. Soc. xxxii. pp. 361-373 (1920).

† They do involve, however, an additional measurement of temperature at some point on the rod itself.

- (3) A particular case of (1), applicable to many metallic systems, and leading to the approximate expressions of Section I.
- (4) To find  $k$ , given the dimensions of the rod, the amount of heat supplied to one end per second, and the temperatures of the two ends.
- (5) To find  $k$ , given the ratio of the heat supplied to the temperature of the hot end for two different lengths of the same rod.
- (6) To find the emissivity  $h$  directly, given the same data as in (4) above.

The experimental conditions are assumed to be similar to those used in the paper referred to in Section I.

The quantities used in the calculations are defined as follows:—

$l$  = length of the rod, in cms.

$r$  = radius of a rod of circular cross-section, in cms.

$q$  = area of cross-section, in cms.

$p$  = perimeter of the rod, in cms.

$h$  = emissivity of the rod surface—*i. e.*, the number of calories emitted per sq. cm. per degree cent. of temperature difference.

$k$  = coefficient of thermal conductivity of the material.

$\alpha = \sqrt{hp/qk}$ .

$H$  = the number of calories supplied per second to the hot end of the rod.

$V$  = the temperature difference in degrees cent. between the hot end of the rod and its surroundings.

$V'$  = the same, for the cold end of the rod.

$x$  = the temperature difference between a point  $x$  cms. from the hot end of the rod and the surroundings.

(1) To find  $k$ , given  $p$ ,  $q$ ,  $l$ ,  $H$ ,  $V$ ,  $v$ , and  $x$ .

The general equation for the fall of temperature along a rod in the condition specified is

$$\frac{d^2v}{dx^2} = \frac{hp}{qk} v = \alpha^2 v, \quad \dots \dots (1)^*$$

of which a general solution is

$$v = A \cosh \alpha x + B \sinh \alpha x, \quad \dots \dots (2)$$

where  $A$  and  $B$  are constants.

\* " $h$ " is assumed to be constant in this equation, and the method given below will only hold for cases in which the fall of temperature along the rod is limited to a few degrees.



To determine the values of A and B, put  $x=0$  ;

then  $v=V$ , and therefore  $A=V$ .

Also when  $x=0$ ,

$$H = -kq \left( \frac{dv}{dx} \right) : \therefore \frac{dv}{dx} = -\frac{H}{kq},$$

and by differentiating (2),

$$\begin{aligned} \frac{dv}{dx} &= \alpha A \sinh \alpha x + \alpha B \cosh \alpha x \\ &= \alpha B \text{ when } x=0. \end{aligned}$$

Hence

$$\alpha B = -\frac{H}{kq}.$$

$$\therefore B = -H/kq\alpha ;$$

$$\therefore v = V \cosh \alpha x - \frac{H}{kq\alpha} \sinh \alpha x \quad . \quad . \quad . \quad (3)$$

$$\text{and} \quad \frac{dv}{dx} = \alpha V \sinh \alpha x - \frac{H}{kq} \cosh \alpha x. \quad . \quad . \quad . \quad (4)$$

Now put  $x=l$ . Then  $v=V'$  ; so that

$$V' = V \cosh \alpha l - \frac{H}{kq\alpha} \sinh \alpha l \quad . \quad . \quad . \quad (5)$$

$$\text{and} \quad \frac{dv}{dx} = \alpha V \sinh \alpha l - \frac{H}{kq} \cosh \alpha l. \quad . \quad . \quad . \quad (6)$$

But when  $x=l$ , the heat transmitted by conduction through the end layer of the rod is identical with that emitted from the surface of that end.

Therefore when  $x=l$ ,

$$-kq \frac{dv}{dx} = hqV' ;$$

i. e., when  $x=l$ ,

$$\frac{dv}{dx} = -\frac{hV'}{k} = -\frac{hp}{qk} \cdot \frac{qV'}{p} = -\frac{q\alpha^2}{p} \cdot V'$$

Substituting from (5) and (6),

$$\alpha V \sinh \alpha l - \frac{H}{kq} \cosh \alpha l = -\frac{q\alpha^2}{p} \left( V \cosh \alpha l - \frac{H}{kq\alpha} \sinh \alpha l \right).$$

Multiplying throughout by  $pkq \operatorname{sech} \alpha l$ ,

$$pqk\alpha V \tanh \alpha l - pH = -kq^2\alpha^2 V + q\alpha H \tanh \alpha l,$$

which on rearrangement gives

$$k = \frac{H}{q\alpha V} \cdot \frac{q\alpha \tanh \alpha l + p}{q\alpha + p \tanh \alpha l} \quad \dots \quad (7)$$

$$\text{or} \quad k = \frac{H}{q\alpha V} \coth \left( \alpha l + \tanh^{-1} \frac{q\alpha}{p} \right). \quad \dots \quad (8)$$

From (3),

$$kq\alpha v = kq\alpha V \cosh \alpha x - H \sinh \alpha x;$$

$$\therefore k = \frac{H}{q\alpha V} \cdot \frac{\sinh \alpha x}{\cosh \alpha x - v/V}. \quad \dots \quad (9)$$

Combining (8) and (9), we have the relation

$$\frac{\sinh \alpha x}{\cosh \alpha x - v/V} = \frac{q\alpha \tanh \alpha l + p}{q\alpha + p \tanh \alpha l} \quad \dots \quad (10)$$

$$= \coth \left( \alpha l + \tanh^{-1} \frac{q\alpha}{p} \right). \quad \dots \quad (11)$$

Now, while an explicit expression for  $\alpha$  cannot be obtained, it is quite a simple matter to evaluate it graphically. All the quantities are known except  $\alpha$ ; so that, by giving  $\alpha$  a few arbitrary values, it is possible to plot out the curves

$$\frac{\sinh \alpha x}{\cosh \alpha x - v/V} = f(\alpha), \quad \text{and} \quad \frac{q\alpha \tanh \alpha l + p}{q\alpha + p \tanh \alpha l} = F(\alpha),$$

and this may be done with any degree of precision. The value of  $\alpha$  at the point of intersection of the two curves is the value which satisfies the relations (10) and (11). The other coordinate at the point of intersection gives the value of  $f(\alpha)$  or  $F(\alpha)$  at that point. The value of  $k$  now follows by simple substitution in (9).

It will be observed that this solution is quite general, and does not involve the measurement of  $h$ . A numerical example will illustrate the method.

*Example :—*

A cylindrical wire 10.00 cm. long and 2 mm. thick is placed in a constant temperature enclosure and heated at one end at the rate of  $6.290 \times 10^{-3}$  calorie per second. When equilibrium is reached, the hot end is found to be  $50.00^\circ \text{C}$ . hotter than the enclosure, while at a point 7.31 cm. from the hot end the temperature is  $0.83^\circ \text{C}$ . above that of the enclosure.

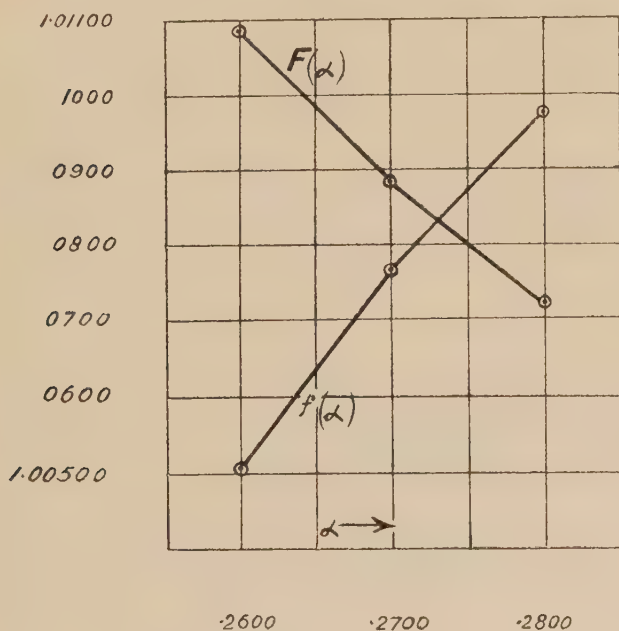
We have the following data :—

$$r=0\cdot100, \quad p=0\cdot6283, \quad q=0\cdot03142, \quad l=10\cdot00,$$

$$H=6\cdot290 \times 10^{-3}, \quad V=5^{\circ}00 \text{ C.}, \quad v=0^{\circ}83 \text{ C.}, \quad x=7\cdot31.$$

TABLE of values of  $\alpha$ ,  $f(\alpha)$ , and  $F(\alpha)$ .

$\alpha$ .	$qa/p$ .	$\alpha x$ .	$al$ .	$\cosh \alpha x$ .	$\sinh \alpha x$ .	$f(\alpha)$ .	$\tanh al$ .	$F(\alpha)$ .
·2600	·0130	1·9006	2·6000	3·4197	3·2702	1·00508	·98903	1·01081
·2700	·0135	1·9737	2·7000	3·6681	3·5292	1·00773	·99101	1·00883
·2800	·0140	2·0468	2·8000	3·9361	3·8070	1·00977	·99263	1·00722



The two curves intersect at the point  $\left\{ \begin{array}{l} \alpha = \cdot2728 \\ f(\alpha) = 1\cdot00835 \end{array} \right\}$   
 (see Curve), from which it follows, since  $k = \frac{H}{qaV} \cdot f'(\alpha)$ , that

$$k = \frac{6\cdot290 \times 10^{-3} \times 1\cdot00835}{0\cdot031416 \times 0\cdot2728 \times 5},$$

$$\underline{k=0\cdot148(0)}.$$

We now proceed to two particular cases of the above.

(2) *A particular case of (1) when  $l$  is large.*

When  $l$  is great,  $\tanh \alpha l$  approximates to unity, and it follows from (7) that  $k = \frac{H}{q\alpha V}$ .

Hence by (10), 
$$\frac{\sinh \alpha x}{\cosh \alpha x - v/V} = 1;$$

$$\therefore v/V = \cosh \alpha x - \sinh \alpha x = e^{-\alpha x};$$

$$\therefore \alpha x = \log_e (v/V);$$

$$\therefore \alpha = -\frac{1}{x} \log \frac{v}{V} = \frac{1}{x} \log \frac{V}{v}.$$

$$\therefore k = \frac{H}{q\alpha V} = \frac{Hx}{qV \log_e \frac{V}{v}}, \quad . \quad . \quad . \quad . \quad (12)$$

a very simple expression, independent of  $h$ , and requiring the measurement of the heat  $H$  given to one end of the rod, the temperature  $V$  at that end, the cross-sectional area of the rod, and the temperature  $v$  at a point distant  $x$  from the hot end.

(3) *A particular case of (1), assuming  $h/k\alpha$  is small.*

It was shown in a former paper (*loc. cit.*) that for a great many thin metallic rods the quantity  $h/k\alpha$  is very small, the error involved in neglecting it being less than one part in ten thousand. Making this approximation, we have

$$\frac{q\alpha}{p} = \frac{q\alpha^2}{p\alpha} = \frac{q}{p\alpha} \cdot \frac{hp}{kq} = \frac{h}{k\alpha} = 0.$$

Therefore, substituting in (8) and (11),

$$k = \frac{H}{q\alpha V} \coth \alpha l \quad . \quad . \quad . \quad (13)$$

$$\text{and} \quad \frac{\sinh \alpha x}{\cosh \alpha x - v/V} = \coth \alpha l. \quad . \quad . \quad . \quad (14)$$

This greatly simplifies the graphical solution of (11). It will be observed that in the numerical example given above the tabulated values of  $F(\alpha)$  are very nearly the reciprocals of those of  $\tanh \alpha l$ . The error involved in writing  $F(\alpha) = \coth \alpha l$  would be only 0.2 per cent. of the value of  $k$ ,



The formula quoted at the beginning of this paper follows directly from the relation

$$k = \frac{H}{q\alpha V} \coth \alpha l,$$

for

$$k^2 = \frac{H^2 \coth^2 \alpha l}{q^2 \alpha^2 V^2}$$

$$= \frac{H^2 \coth^2 \alpha l}{q^2 \frac{hp}{qk} \cdot V^2} = k \frac{H^2 \coth^2 \alpha l}{pqhV^2}.$$

$$\therefore k = \frac{H^2}{pqhV^2} \cdot \coth^2 \alpha l. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

(4) To find "k" from measurements of  $q, l, H, V$ , and  $V'$ , with the assumption as in (3) that the quantity  $qa/p$  is small.

From (14)

$$\frac{\sinh \alpha x}{\cosh \alpha x - v/V} = \coth \alpha l.$$

When  $x=l$ , and  $v=V'$ ,

$$\sinh^2 \alpha l = \cosh^2 \alpha l - \frac{V'}{V} \cosh \alpha l;$$

$$\therefore \frac{V'}{V} \cosh \alpha l = \cosh^2 \alpha l - \sinh^2 \alpha l = 1.$$

$$\therefore \cosh \alpha l = \frac{V}{V'}. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\therefore \alpha = \frac{1}{l} \cosh^{-1} \left( \frac{V}{V'} \right), \quad . \quad . \quad . \quad . \quad . \quad (17)$$

while

$$\sinh \alpha l = \frac{\sqrt{V^2 - V'^2}}{V'} \quad \text{and} \quad \coth \alpha l = \frac{V}{\sqrt{V^2 - V'^2}}. \quad (18)$$

Since (13),

$$k = \frac{H}{q\alpha V} \coth \alpha l,$$

by (17) and (18)

$$k = \frac{H}{qV} \cdot \frac{l}{\cosh^{-1}(V/V')} \cdot \frac{V}{\sqrt{V^2 - V'^2}}$$

or

$$k = \frac{Hl}{q \sqrt{V^2 - V'^2} \cdot \cosh^{-1}(V/V')}.$$

(5) To find " $k$ ," given the ratio  $H/V$  for two values of  $l$ .

$$\text{Since} \quad \frac{H_1}{qaV_1} \coth \alpha l_1 = k = \frac{H_2}{qaV_2} \coth \alpha l_2,$$

$k$  can be found graphically in a manner entirely analogous to that used in I. (1) by plotting the two functions  $\frac{H}{qaV} \coth \alpha l$  against  $\alpha$  and taking their value at their point of intersection.

(6) To find " $h$ ," given  $p, q, l, H, V$ , and  $V'$ , when  $\frac{qc}{p}$  is small.

$$\text{Since by definition } a^2 = \frac{hp}{kq}.$$

$$\therefore hp = qa^2k,$$

which by (13)

$$= qa^2 \frac{H}{qaV} \coth \alpha l = \frac{H\alpha \coth \alpha l}{V}.$$

Therefore by (17) and (18),

$$\begin{aligned} h &= \frac{H}{pV} \cdot \alpha \coth \alpha l \\ &= \frac{H}{pV} \cdot \frac{1}{l} \cosh^{-1} \left( \frac{V}{V'} \right) \cdot \frac{V}{\sqrt{V^2 - V'^2}} \end{aligned}$$

$$\text{or} \quad h = \frac{H \cosh^{-1} (V/V')}{pl \sqrt{V^2 - V'^2}}.$$

In Section III. (4), (5), and (6), perfectly general solutions making no restriction on the magnitude of  $qa/p$  are readily available by the same method, but the forms obtained are rather involved.

Our thanks are due to Prof. C. H. Lees for kindly advice and criticism.

XXXV. *The Thermal Theory of Gas Ignition by Electric Sparks.* By J. D. MORGAN, *M.Sc.* \*

*Introduction.*

THE main purpose of this paper is to examine the thermal theory of gas ignition by electric sparks in the light of experimental results. The theory asserts that ignition depends on the raising of a sufficient volume of the combustible gas to a sufficient temperature. Two quantities only are involved in the theory—volume and temperature. No account is taken of chemical or material changes in the process of ignition. The justification for the reference to volume is that a spark insufficient to initiate combustion of the whole of the gas will burn some of the gas immediately adjacent to the spark, but the flame does not spread. It appears to be necessary to ignite a sufficient quantity of the gas to ensure autogenous ignition of the whole. From the theory as stated, it follows that to cause ignition requires a definite amount of heat to be imparted to a definite volume of the gas. If that volume could be raised instantly and uniformly to the ignition temperature, without loss of heat to the surrounding gas, the amount of heat necessary to cause ignition would be the minimum. Experimental results can only approximate to the ideal minimum, and the degree of approximation will depend on conditions associated with the experiment. Diversity of results is therefore inevitable.

The fact that the subject of spark ignition is associated with experimental results of great diversity forms the basis of the opinion held by some, that but little if any satisfactory information exists on the subject. It is not generally understood, however, that diversity as regards the energy required to cause ignition is inevitable, and is at the same time consistent with the simple hypothesis above enunciated.

By means of the thermal theory much of the perplexity which surrounds the subject of spark ignition is caused to disappear, and apparently discordant results are co-ordinated. There is no alternative theory of which the same can be stated. The suggestion has been made that ignition depends upon some form of electrical activity which cannot be expressed in terms of energy, but the suggestion does not appear to have been developed. It is not denied that the interaction of the spark and gas may be electrical in character. This possibility is not excluded by the thermal theory, any more than is an electrical theory of flame excluded by the science of thermodynamics.

\* Communicated by Prof. E. Taylor Jones.

*Experimental limitations.*

Before a clear conception of the subject can be formed it is necessary to know something of the experimental limitations. The supposition that ignition is an operation depending on the transference of energy to the gas from the spark in the form of heat is not unreasonable. Until the supposition is proved to be false, measurements of energy, or of factors involved in appropriate energy expressions, afford the natural means of investigation. It will be obvious that three measurements are conceivable, though it will be apparent that only two are possible. As a result of the spark a temperature wave travels from the spark throughout the gas. Ignition follows from a transient condition in which the heat given up by the spark is localized in the region surrounding the spark. A direct attack upon the problem would involve a measurement of the heat concentrated in the gas region adjacent to the spark immediately prior to ignition, but this is impossible. A practicable method is to measure the heat given up by the spark, the heat being imparted for the purpose of measurement to a non-inflammable gas. Only the final effect of the heating can be measured in this way,—not the transient condition on which ignition depends. The method has been used. It is inconvenient, and possesses no advantages, except as a check, over the other and third method which is the one ordinarily employed. This consists in measuring the energy (or a suitable factor of the energy) available for spark production in the apparatus used for generating the spark.

The use of the energy available for spark production as a criterion of incendivity (or ability of the spark to cause ignition) involves several arbitrary assumptions. It tends to produce a crop of misleading results, and depends more on necessity than choice. Nevertheless, provided its limitations are always kept in view, the method is of great value, and by its aid a clear appreciation of the conditions affecting ignition becomes possible.

The sparks used in ignition experiments are divided into two classes, inductance and capacity sparks. Inductance sparks are obtained between a pair of contacts when the current flowing in an inductive circuit is interrupted by separation of the contacts. Capacity sparks result from the discharge of an electrostatic condenser across a gap between a pair of electrodes. The energy available for the production of an inductance spark is equal to  $\frac{1}{2}Li^2$ , where  $L$  is the inductance of the circuit and  $i$  the current flowing prior to interruption. For a capacity spark,  $\frac{1}{2}CV^2$  is the measure of the energy available for spark production,  $C$  being the



capacity of the condenser and  $V$  the sparking voltage of the gap. The use of either measurement involves the assumption that the whole or the greater part of the energy available is discharged in the spark. Under suitable experimental conditions a great, if not the greater, part of the energy undoubtedly appears in the spark, and the proportion is sufficiently definite and constant to justify the use of available energy as a measure (for comparative purposes) of actual spark energy. But under unfavourable experimental conditions the assumption leads to anomalous results; examples of such conditions are given in the later portion of this paper.

*Principal causes of Spark Energy Variations.*

Assuming satisfactory experimental conditions, diversity in the spark energy required to cause ignition of a given gas results mainly from one or both of two conditions. The one depends on the rate at which the heat is imparted to the gas, the other on the manner in which the electrodes, between which the spark is formed, interfere with the efficient distribution of heat in the gas adjacent to the spark.

*Effect of rate of imparting Heat from Spark to Gas.*

The heating of the gas to the condition required for ignition involves time. During this time heat is accumulating in the region around the spark, and some is also passing uselessly to the remoter portions of the gas. At the instant of ignition the temperature distribution in the gas around the spark is not uniform. Of the quantity of heat given by the spark to the gas, the amount that is effectively employed in causing ignition will depend on the rate at which the heat is imparted. This aspect of the problem has been examined theoretically in a previous paper\*. In that paper the problem was reduced to one of examining the heating effect of different point sources of heat on air, the heat being communicated from the source to the air by conduction only. The calculations showed that the effectiveness of a given quantity of heat in raising a given volume of gas to a given temperature depends essentially on the manner in which that heat is communicated to the gas. When the heat is imparted instantaneously to a point source, the boundary of a larger volume of gas is raised to a given temperature than when the same quantity of heat is imparted at a uniform rate over a finite interval of time. For

\* "On the form of the temperature wave spreading by conduction from point and spherical sources; with a suggested application to the problem of spark ignition." Taylor Jones, Morgan & Wheeler, Phil. Mag. vol. xliii. Feb. 1922.

example, the heating effect of a point source of total heat of 0·001 calorie uniformly in action over 0·005 sec. (continued heat source) was about 17 per cent. less than that of an instantaneous point source of the same total heat. In the calculations it was assumed that the different point sources of heat were surrounded entirely by gas.

It is difficult, indeed it appears impossible owing to the complex conditions which exist in the ignition of a gas by a spark, to test directly the conclusions arrived at in that paper, although it is known that, in general, the incendivity of inductance sparks (which can be regarded as continued heat sources) is less than that of capacity sparks (which can be regarded as instantaneous heat sources). For example, in some experiments, the least energy by which ignition of an 8·5 per cent. methane-air mixture could be obtained by a capacity spark was ·002 joule. That for an inductance spark was ·006 joule. It is not possible, however, to state whether the difference was due wholly or only in part to the rate of heating, because both results depend to some extent on the "electrode effect" described below. The general conclusions arrived at in the earlier paper are, however, equally applicable to another ignition problem in connexion with which they are easily tested in a direct manner. For the ignition of explosives in blasting operations, electrically fired fuseheads are commonly used. A fusehead consists of a solid globule of readily ignitable material in which is embedded a very fine and short wire. Ignition of the fusehead is effected by passing an electric current through the wire. Experiments on the ignition of fuseheads are very much simpler than those on the ignition of gases, as the conditions are more definite. In the experiments to be mentioned the object was to find the current required for ignition when the duration of current was limited to a definite interval of time. The results obtained in one set of experiments on fuseheads of 1 ohm resistance are given below :—

Duration of current. sec.	Igniting current. amp.	Energy required for ignition. $C^2R.t.$
·1	·38	·0144
·08	·4	·0128
·06	·415	·0103
·04	·44	·0077
·03	·48	·0069
·02	·53	·0056
·01	·66	·0044
·005	·89	·004

The results when plotted give a straight line relationship between  $W$  and  $t$ , where  $W$  = energy and  $t$  = time. Calculations made by Prof. E. Taylor Jones, based on the assumptions made in the previous paper, also show that the relation between  $W$  and  $t$  should (in the case of a point source) be linear over the same range of values of  $t^*$  as that in the above table. The results obtained in the fusehead experiments therefore agree well in this respect with the thermal theory of ignition.

There appears to be no reason for supposing that, as a thermal operation, the heating of a combustible gas by a hot vapour is essentially different from the heating of a combustible solid by a hot wire. In view of the direct evidence cited, and the absence of evidence to the contrary, it must be regarded as established that the effectiveness of a spark as an igniting agent depends on the rate at which it imparts heat to the gas, and that the differences which are known to exist between the incendivities of capacity and inductance sparks are due in part to this cause.

### *Electrode Effect.*

In the light of the calculations of the first paper, another aspect of the subject has been treated experimentally †. The object was to find what modifying effect could be attributed to the presence of electrodes on the heat required to cause ignition of the gas, ignition being initiated by a spark in the region between the electrodes. It was found that the effect of the electrodes on the spark energy necessary for ignition was very great. Using capacity sparks (which can be regarded as instantaneous heat sources) and rather blunt electrodes presenting hemispherical surfaces to the gap, .007 joule was required to cause ignition of an 8.8 per cent. methane-air mixture when the gap width, or distance between the electrodes, was 0.31 inch. Increasing the gap width to 0.55 inch, and thereby increasing the volume of gas between the electrodes, the energy required for ignition was only .002 joule. It was found that the relationship between these and intermediate figures was consistent with calculations derived from those of the previous paper. Changes in the shape of the electrodes

\* The calculations show that at very small values of  $t$  the energy  $W$  varies slightly less rapidly than according to the linear relation which holds at larger values.

† "Some observations on the ignition of combustible gases by electric sparks," J. D. Morgan, *Phil. Mag.* vol. xlv. May 1923.

were also accompanied by consistent variations in the energy required for ignition. Change of material appeared to have no effect, as might be expected. The experiments described in the second paper established a fact of great practical importance, namely, that the presence of electrodes can cause very large variations in the amount of heat energy necessary for the ignition of a given gas. They also show that such variations accord with the supposition that ignition depends upon a thermal process.

### *Inductance Sparks.*

More recently the problem has been examined from various other view points with inductance sparks. It is known that the incendivity of such sparks is lower than that of capacity sparks. This is attributable to two causes. In the first place, the sparks are of appreciable duration and are therefore less efficient as heating agents than the approximately instantaneous capacity sparks. In the second place, the sparks are initiated in a much more confined or restricted gas region than capacity sparks. Stated otherwise, the electrode effect may be much greater in the one case than the other; although it should be mentioned that when capacity sparks are produced between electrodes which are very close together the energy required for ignition approaches very nearly, and has been found to exceed, that necessary with inductance sparks. For example, as already stated, the energy required in a capacity spark formed in a gap of  $\cdot 031$  inch wide, to ignite an 8.8 per cent. methane-air mixture, was  $\cdot 007$  joule. Ignition of the same mixture with an inductance spark has been obtained with a spark energy of as low as  $\cdot 006$  joule. But by slowing down the rate of break, or by increasing the area of adjacent electrode surfaces, this figure can be greatly increased owing to increase of electrode effect. It can also be increased by making the rate of break very rapid; the electrode effect is then reduced to the minimum, but the energy that actually appears in the spark is diminished, owing apparently to premature extinction of the spark. But when an inductance spark produced under optimum conditions is compared with a capacity spark also produced under optimum conditions, the energy required for ignition by the inductance spark is greater than that required by a capacity spark.

The energy required to produce an inductance spark is represented by the quantity  $\frac{1}{2}Li^2$ . It is important to consider what results are to be expected from experiments in which



$L$  and  $i$  are varied, the rate of separation of the contacts and the composition of the gas mixture being kept constant. As a matter of observation, it is known that the sparks required to ignite a given gas vary but little in length and, consequently, in duration over a fairly wide range of variation of  $L$  and  $i$ . With large differences in  $L$  (and corresponding differences in  $i$ ) there is an appreciable difference in the length of the sparks, the sparks obtained with the larger values of  $L$  being longer and less bright than those obtained with small values of  $L$ . Considering first the condition in which there is no appreciable variation of spark length and duration: if the thermal hypothesis is correct, then, under that condition, the product  $\frac{1}{2}Li^2$  should remain constant, because the mean rate at which heat is generated in the spark is then constant. This conclusion is in accordance with experiments\*. Recently the matter has been re-examined, using two air-core coils of different inductance. The gas was a methane-air mixture of 8.5 per cent. methane. The contact breaker consisted of a small flexible phosphor-bronze blade which could be brought into contact with one face of a fixed contact of wedge-shaped section, and after slight flexure could flick past the edge of the fixed contact. This simple device enabled a constant rate of break to be obtained very conveniently. The results were as follows:—

Inductance of coil ( $L$ ).	Current prior to break ( $i$ ).	Energy to provide igniting sparks ( $\frac{1}{2}Li^2$ ).
(1) .02144	.77	.00635
(2) .012	1.025	.00630

In these experiments the difference between the two inductances is not nearly so large as the differences employed in the earlier experiments, but is sufficient to establish the point under consideration.

In the other condition, in which there are appreciable differences in the spark lengths (and consequently durations), the experimental conditions are obviously more complicated. The greater brightness of the shorter sparks indicates a more rapid rate of heat generation. If this were the only differentiating feature in the experiments, the product  $\frac{1}{2}Li^2$  should have been less with a small value of  $L$  than with a large value. On the other hand, the longer sparks obtained with

\* "The ignition of explosive gases by electric sparks," J. D. Morgan, *Trans. Chem. Soc.* 1919, vol. cxv.

the larger values of  $L$  should have been more effective on account of the diminution of electrode effect, and the product  $\frac{1}{2}Li^2$  should have been less with the large values of  $L$  than with the small values. Actually, in the first experiments cited, it was found that with very large differences of  $L$  the product  $\frac{1}{2}Li^2$  remained constant, due, no doubt, to the fact that differences in the rate of heating were accompanied by counteracting differences in the electrode effect.

In some recent experiments with inductance sparks by Prof. R. V. Wheeler, the following figures were obtained in the ignition of an 8.5 per cent. methane-air mixture.

Applied volts.	Inductance, henry.	Igniting current, amp.	Spark energy, ( $\frac{1}{2}Li^2$ ) joule.
90	.031	.42	.0027
"	.063	.26	.0021
"	.095	.19	.0017
30	.063	.35	.0038

It will be noticed that the results differ from the writer's in that the energy required for ignition is much smaller, and the product  $\frac{1}{2}Li^2$  diminishes with increase of inductance. It will also be noticed that at the lower applied voltage (30) the spark energy with an inductance of .063 henry rises from .0021 to .0038. In the author's experiments the applied voltage was 4. The two sets of results are hardly comparable, for the reason that the high voltage used in Wheeler's experiments causes considerable energy to be given to the spark which is not included in the quantity  $\frac{1}{2}Li^2$ . This point is discussed later. For comparison with Wheeler's results, the following obtained recently by the author, in experiments on 8.5 per cent. methane-air mixture with high impressed voltage, are of interest.

Impressed volts.	Inductance, henry.	Igniting current, amp.	Spark energy ( $\frac{1}{2}Li^2$ ).
(1) 220	.02144	.35	.00130
(2) 220	.012	.4	.00096

Here the spark energy increases with increase of inductance. The fact that the variation is the reverse of Wheeler's is no doubt due to some difference in the experimental conditions. Whatever the explanation, the results obtained with high impressed voltage afford no evidence for or against the thermal theory, for the reason already given. The results obtained in experiments with low impressed voltage

show that the behaviour of inductance sparks accords with the thermal theory of ignition.

*Inductance Sparks produced in Alternating Current Circuits.*

In consequence of the work of Thornton there is a widespread belief that sparks produced in alternating current circuits are much less effective in causing ignition than sparks produced in direct current circuits. It has been alleged that his experiments disprove the thermal theory of ignition, and it has also been advocated that where danger from gas ignition is to be anticipated, it is preferable to employ alternating current on account of the wider margin of safety that it is supposed to give. The matter is of great practical importance, and it also has an important bearing on the theoretical aspect of the subject of spark ignition. It is quite easy to show that the belief is without foundation in fact. A small alternator giving a good sine wave was arranged in a circuit containing the ignition apparatus, an air-core inductance coil, a resistance, and a hot wire ammeter. Provision was made for including in series with the circuit a small accumulator as a source of direct current. In the direct current experiments, the alternator rotor was fixed in the position of maximum inductance, and the current from the battery was adjusted until the spark obtained on breaking the circuit was able to ignite the gas. Subsequently the battery was removed from the circuit and current was generated by the alternator, the resistance of the circuit remaining the same. The excitation of the alternator was varied until the least igniting spark was obtained. The flick contact-breaker above mentioned was actuated by hand, and consequently the necessary coincidence of the break with the peak of a current-wave was a matter of chance. But by repeated trials and frequent changes of gas in the explosion-chamber, the least current required to produce an igniting spark was determinable without great difficulty. The procedure may appear to be crude, but actually it is free from the possibility of any serious error. The results of experiments on an 8.5 methane-air mixture were as follows :—

Direct current required to produce igniting spark .415 amp.

Alternating current required to produce igniting spark :—

Periodicity.	r.m.s. current.	Peak current.
68	.29 amp.	.41
200	.3 „	.42

It will be apparent that the results for alternating and direct current are practically the same. The arrangement of the experiment was such as to insure as nearly as possible identical conditions for the two currents. With the alternator running there was no doubt a small variation in the effective inductance of the generating windings, and this probably accounts for the small differences found in the igniting currents. The experiments establish the fact that there is no difference in the effectiveness of alternating and direct current sparks when produced under similar conditions. Prof. Wheeler has informed the writer that he also has experimented with the two kinds of currents, and found no essential difference in the incendivity of the sparks produced by them.

*Thornton's "Ionization" Test.*

In a recent paper \* Prof. Thornton has given an account of an experiment intended apparently to dispose of the thermal theory of ignition. His words are as follows :—

"The statement has been made here that ignition is electrical rather than thermal. As a test of this in the case of break sparks the following experiment was made. The least igniting current of a 35 per cent. hydrogen-in-air mixture was found by trial at 200 volts, 250 p.p.s. to be 0.4 ampere. The same poles were then sparked in pure hydrogen to remove oxide or occluded oxygen, and it was then found that the explosive mixture could not be ignited with less than 6 amperes broken. The sparks were large and bright but were electrically inert though their thermal value was many times greater than before. The first step in ignition is the formation of active oxygen ions. There is no difference between hydrogen and other gases except in sensitiveness to spark ignition."

It will be noticed that Prof. Thornton used alternating current for the production of his spark. Judging from the current values given he also used a non-inductive circuit. Seeing that the essential feature of the Thornton experiment lies in the "sparking" in pure hydrogen between the ignition experiments, the results should be independent of other factors. Consequently, in order to insure a high degree of precision, the author tried the experiment with a small air-core inductance in the circuit and used direct current.

\* "Researches on the safe use of electricity in Coal-mines," W. M. Thornton, Journ. Inst. Elect. Engin. vol. lxii. No. 330 (June 1924).



Experiments were repeated many times with hydrogen-air, methane-air, and coal gas-air mixtures, but in every case the current required for ignition was the same before and after sparking in hydrogen.

### *Experimental Irregularities.*

It will be apparent that before the results of any ignition experiments can be admitted as having any theoretical value, the conditions under which the experiments are conducted must be rigorously investigated. The principal reason for this arises from the necessity for using  $\frac{1}{2}Li^2$  or  $\frac{1}{2}CV^2$ , or one of the factors in those expressions, as a measure of the spark energy. In inductance spark experiments the quantity  $\frac{1}{2}Li^2$  may give a figure differing greatly from the actual value of the energy imparted to the spark. Sometimes the figure is greater than the true figure, due, for example, to losses in the spark-producing system. Sometimes it is much less, due, for example, to extra, or unmeasured, energy being given to the spark from the current source, as when a high impressed voltage is used. In some experiments the inductive portion of the spark-producing system was varied. A coil was mounted, in the first instance, on one of the limbs of a laminated iron frame. When the current was adjusted to give an igniting spark,  $\frac{1}{2}Li^2$  was equal to .0023 joule. Then the same coil was mounted on a core in the form of a straight laminated iron bar. Under this condition ignition was obtained when  $\frac{1}{2}Li^2$  was equal to .0008 joule. Finally all iron was removed from the coil, giving an air-core, and the value of  $\frac{1}{2}Li^2$  for ignition then became .0006 joule. In all other particulars the experimental conditions were the same. Subsequent measurements, in a special calorimeter, of the heat actually dissipated in the sparks showed that the heat content of the sparks produced under the three different conditions was the same. The differences in the measured values of  $\frac{1}{2}Li^2$  were due to core losses. Owing to the difficulty of standardizing an inductive system involving iron it is advisable to use air-core coils.

A well-known result in experiments with inductive sparks is that the energy required for ignition of a given gas (as measured by  $\frac{1}{2}Li^2$ ) diminishes with increase of impressed voltage. The spark-producing system must include a source of electromotive force for supplying the requisite current. When the contacts are together, the voltage across them is practically zero. On separation the rise of voltage across

the contacts depends not only on the inductive voltage, which first rises and afterwards falls, but also on the impressed voltage due to the source, which rises from zero to a maximum and persists. During the passage of the spark, energy is derived from both the stored magnetic energy of the system and the source, and the contribution from the latter, which may be large, is not included in the measurement of  $\frac{1}{2}Li^2$ . In one experiment using an air-core coil, for which  $L = \cdot 0214$  henry, the current required to produce a spark capable of igniting an 8.5 per cent. methane-air mixture was .77 amp. ( $\frac{1}{2}Li^2 = \cdot 0063$ ), the voltage of the battery from which current was derived being 4 volts. Applying 220 volts to the system, the current required to produce an igniting spark, all other factors in the experiment being the same, was .35 amp. ( $\frac{1}{2}Li^2 = \cdot 0013$ ). Check experiments showed that the heat delivered to the spark was the same in the two cases, and the apparent difference of incendivity was due solely to the fact that the measure,  $\frac{1}{2}Li^2$ , does not take into account that contribution from the source which augments and tends to maintain the spark. In all work of a theoretical character on the incendivity of inductance sparks it is necessary to keep the impressed voltage as low as possible so that the energy derived directly from the source of current is negligible.

Capacity sparks, as already stated, are usually defined by the expression  $\frac{1}{2}CV^2$ . Here also difficulties are encountered. The charge given to the condenser is not wholly discharged across the spark-gap, although, under suitable conditions, the amount remaining in the condenser after the spark has passed is small and bears a definite relationship to the total charge. Using condensers with solid dielectrics, the residual charge may be relatively high, and what is worse, it is often irregular. In some experiments with glass condensers, the calibration curve giving the relationship between voltage and quantity of current discharged across the spark-gap showed well-marked steps. Mica and rubber were also found to be unsatisfactory. The most accurate results are obtained with air condensers, the charge remaining in the condenser after the spark has become extinct being small and regular.

Sparking voltage is a quantity which is often very erratic. When exposed to the open air of a room the sparking voltage of a given gap across which the voltage is raised gradually may be remarkably regular, but when contained in a small explosion chamber, voltages of as much as twice the normal

break-down voltage have been observed before the spark occurred. It cannot be assumed, therefore, unless precautions are taken, that a spark-gap set to breakdown at a given voltage will always spark over at that voltage. With proper care, however, very great accuracy and consistency can be obtained when using capacity sparks; in some experiments on methane, the difference in gap width necessary to convert a non-igniting into an igniting spark was within .0005 inch. The above remarks apply to gradually applied voltages, and not to impulsively applied voltages such as are obtained when an ordinary induction-coil or magneto is used. Impulsively applied voltages are so liable to produce irregular and misleading results that they are hardly suitable for use in ignition research unless elaborate precautions are taken.

It is well-known that inductance sparks (or arcs) form more readily between some metals when separated than others. Wheeler has investigated this aspect of the subject, and finds that the energy required to produce a spark capable of igniting a given gas increases with the vaporization temperature of the metals used in the contacts. The proportion of the available energy which appears as heat in the spark diminishes with increase of vaporization temperature, consequently when a metal like platinum is used in the contacts, a larger current is required to give an igniting spark than when a metal like brass is used, other conditions in the circuit remaining the same. When sparks are produced between permanently separated electrodes (capacity sparks), the material of the electrodes appears to have no effect on the energy required to cause gas ignition.

It will be apparent from the foregoing that a necessary preliminary to any work on spark ignition is a thorough study of the experimental conditions, and until this is done no progress can be made in correlating the diverse results which are inevitably found when the experimental conditions are varied.

### *Summary.*

The thermal theory of spark ignition asserts that ignition depends on the raising of a sufficient volume of the combustible gas to a sufficient temperature. It follows from a mathematical development of the theory that the energy required for ignition of a given gas varies with (a) the rate at which heat is imparted to the gas, and (b) the shape and proximity of the electrodes. The chief points of the present

paper may be summarized by stating the following experimental results which agree with the thermal theory of spark ignition:—

1. The incendivity of capacity sparks is found in general to be greater than that of inductance sparks, in accordance with the theoretical result that a source of short duration is more effective than one in which the heat is supplied over a longer interval.

2. The incendivity of capacity sparks depends upon the shape and relative position of the spark electrodes in a manner to be expected on the thermal theory.

3. The energy required for ignition of a given gas by low-voltage inductance sparks is constant over a wide range of values of self-inductance and current so long as the duration of the spark is constant.

4. There is no difference in the incendivity of inductance sparks produced in direct and alternating current circuits.

5. Experiments on the ignition of highly inflammable solids by means of very short hot wires show that the energy required for ignition increases with diminution of the rate of heating, and that over a wide range a linear relation exists between the energy and the time during which it is supplied.

It has also been shown in the paper that other important variations found in experiments are attributable to the manner in which the spark energy is measured.

XXXVI. *On a Critical Resistance for "Flashing" of Air Discharge-tubes.* By JAMES TAYLOR, B.Sc., Pemberton Fellow, and WILLIAM CLARKSON, M.Sc., Armstrong College, Newcastle-upon-Tyne\*.

*Abstract.*

THE paper deals with a continuation of work on the "flashing" of discharge-tubes and the resistance relations necessary for the maintenance of "flashes." (For diagram of circuit see fig. 1.)

It is shown that there is a "critical" resistance  $R_c$  for the air discharge-tubes used, below which no flashing may be obtained, given by the relation

$$R_c = \frac{E - V_b'}{\psi(V_b')}$$

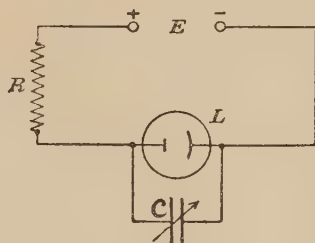
where  $E$  is the charging voltage,  $V_b'$  is the effective lower

\* Communicated by Prof. G. W. Todd, M.A., D.Sc.



critical voltage, and  $\psi$  ( $V_b'$ ) is the current voltage function, under the conditions of the experiments. A tentative explanation of the variation of the voltage intercept for the

Fig. 1.



E, the charging voltage.  
R, the circuit resistance.

L, the discharge-tube.  
C, the capacity shunted across the electrodes.

linear curves between the critical resistance  $R_c$  and the charging voltage E, with the capacity across the discharge-tube, is put forward.

### Introduction.

In a previous paper \* the present writers showed, in the case of the neon discharge-tube or "Osglim" lamp, that there was a critical resistance below which the well-known phenomenon of "flashes" could not be obtained. The relation for this critical value is of the form

$$R_c = \frac{E - V_b}{k(V_b - V_a)}, \quad \dots \quad (1)$$

where E is the charging voltage,  $V_b$  is the lower critical voltage,  $V_a$  the cathode fall of potential approximately, and k the "conductance" of the lamp.

The above relation proceeded out of a simple theory of conduction in the discharge-tube, put forward by one of us in a previous paper †. The condition for no flashes is expressed physically by the fact that during any instant of the discharge through the tube, the quantity of electricity flowing from the condenser is exactly equal to the quantity which flows into the condenser from the charging battery.

In a recent paper on the study of "flashing" in air discharge-tubes some results were put forward tentatively in support of the relation of equation (1). The results were,

\* Taylor and Clarkson, Proc. Phys. Soc. Lond. xxxiv. pt. 4, p. 269.

† Taylor and Clarkson, Journ. Scien. Instrs. i. No. 6, p. 174.

however, neither definite nor conclusive, and a fuller investigation into the problem of the critical resistance of air discharge-tubes was proposed.

Some of the experimental difficulties underlying the investigation were pointed out. In the case of most tubes which are suitable for the investigation of the time relations of flashing, the conductivity is high and consequently the value of  $R_c$  is low. Fairly large currents are thus being carried by the tube at the critical resistances, and this makes for instability, due to the change of conductance and cathode fall with heating, and the intense bombardment of the electrodes by the ions. Furthermore, very serious difficulties are encountered, due to the presence of "salient" points\* (described in another paper) which had the effect of increasing the conductivity of the tube and decreasing the value of the cathode fall of potential.

Very many types of tube were tried, including some with cooled electrodes, but the results were of a disappointing nature. The problem was to obtain a discharge-tube suitable for the production of flashes, but such that its conductance was sufficiently low to give values of  $R_c$  high enough to ensure repeatability and definiteness of results. The electrodes must furthermore be such that no salient points develop and no rapid change in the value of the cathode fall of potential should take place.

The tube most suitable for the experiments consisted of molybdenum or platinum wire electrodes, mounted in small glass stems, parallel to each other. The electrodes were fixed in a bulb of which the walls were sufficiently far removed from the electrodes to minimize "wall effects." The pressure was reduced and the tube "overrun" for several hours with the electrodes red-hot, due to the intense bombardment by the ions; the terminals were reversed from time to time so that each wire in turn was cathode. The tube was finally overrun for a considerable time in one direction. After overrunning in this way, most of the impurities had been removed from the electrodes, and they were in a fairly stable condition†. The tube was judged to be in a stable condition when the anode was covered with a uniform, thin, metal-like deposit, and the discharge spread itself uniformly over the electrodes. Notwithstanding this

\* Salient points are points at which small pieces of impurity (as alkaline salts from sealing-wax &c.) are situate. The presence of these "salient" points causes the discharge to be concentrated upon them, and completely alters the value of  $V_a$  from the normal.

† See also M. E. Dubois, *Comptes Rend.* clxxv. pp. 947-949.

treatment, the discharge-tube constants changed progressively with time and method of treatment, but to a much less extent than in the case of tubes which had not been overrun in this manner.

The preliminary experiments, taken over a wide range of pressures, showed that the  $E, R_c$  graphs were linear, but in the majority of cases intersected the voltage axis at an intercept different from the value  $V_b$  given by the theoretical relation of equation (1).

Since at the majority of pressures used the whole area of the cathode was employed during the luminous period, it was almost certain that the volt-ampere characteristics for the tubes were not of the linear form

$$i = k(V - V_a), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which applied to the case of the neon discharge-tubes\*.

Experiments carried out to check this have not, up to date, been very successful; the majority of the characteristics are, however, almost linear between the lower and upper critical voltages. It therefore became necessary to investigate theoretically the critical resistance function for any volt-ampere characteristic.

*The Generalized Form of the Critical Resistance Function  
for the Discharge-tubes.*

One of us (Taylor) has put forward the following generalized form for the critical resistances:—

If instead of a current-voltage function of the form of equations (2) or (6) we take a perfectly general one of the form

$$i = \psi(V), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the condition for steadiness of the discharge is evidently

$$\frac{E - V}{R} \gtrless \psi(V)$$

or  $R \lessgtr \frac{E - V}{\psi(V)} \quad . \quad . \quad . \quad . \quad . \quad (4)$

If we assume, as is perfectly justifiable from experimental data, that  $\psi(V)$  is a continuous function which increases with increase of  $V$ , we have evidently, if the range of possible

\* Taylor and Clarkson, Journ. Scien. Instrs. i. No. 6, p. 174.

values of  $V$  is from  $V_b'$  to  $V_c$ , that

$$R_c = \frac{E - V_b'}{\psi(V_b')}, \quad \dots \dots \dots (5)$$

where  $V_b'$  is the extinction voltage for the tube under the existing conditions.

Two cases are to be distinguished, viz.:—

(1) In which a portion only of the cathode is employed in carrying the discharge. Under these conditions the cathode fall of potential is constant and remains so until the whole of the cathode is covered by the negative glow.

(2) In which the full area of the cathode is employed during the discharge. Under these conditions an increase of the current density through the tube takes place concurrently with an increase of the voltage across the lamp terminals, and the cathode fall of potential attains values much in excess of the normal.

Under ideal conditions, with parallel plate electrodes, the linear characteristic would now be replaced by a relation of the form proposed by Aston,

$$V = FP^{-1}\sqrt{i} + G, \quad \dots \dots \dots (6)$$

where  $F$  and  $G$  are constants,  $P$  is the pressure of the filling gas,  $V$  the voltage across the tube, and  $i$  the current.

In the tubes used in the present experiments, the full cathodic area was used continuously during the luminous period in flashing, and the work consequently comes under the second case.

#### *The Variation of $V_b$ under different conditions.*

We should expect that if the value of the current through the tube be decreased suddenly, the magnitude of the cathode fall of potential would lag behind the normal value, which would be attained when the conditions become stable.

If  $V_b$  represents, as was suggested in a previous paper\*, the cathode fall of potential plus a voltage just sufficient to carry the ions over to the anode, then the instantaneous value of the lower critical voltage  $V_b'$  will now be greater than the normal value  $V_b$ .

The simple relation of equation (1) for the critical resistance will now be replaced by the more comprehensive one of equation (5). Now it is to be expected that under given

\* Taylor and Clarkson, Journ. Scien. Instrs. i. No. 6, p. 174.



conditions, with a fixed value of the capacity across the electrodes so that a constant quantity of electricity is thrown through the lamp during every luminous period, the function of  $\psi(V_b')$  will also be constant, and the above relation will be linear. The intercept of the  $E, R_c$  graphs with the voltage axis will, however, vary from the normal value  $V_b$  by the divergence of  $V_b'$  from that value.

It is to be expected that  $V_b'$  will depend upon the value of the capacity  $C$  across the discharge-tube terminals, upon the rapidity with which the changes are effected, the nature and condition of the electrodes, and the gas-pressure.

Furthermore, it is reasonable to suppose that there will be a greater lag with currents of high value at the beginning of the luminous period than with currents of smaller initial value. The current at the beginning of the luminous period is, of course, a function of the upper critical voltage  $V_c$ , and will evidently—for a given discharge-tube—be greater the greater the value of  $V_c$ . It is therefore necessary to ascertain whether there is any variation of  $V_c$  with the value of the capacity  $C$ .

#### *The Variation of $V_c$ with the Capacity $C$ .*

The variation of  $V_c$  may be considerable.  $V_c$  has a higher value initially than when the discharge has just ceased, and is furthermore somewhat lower when rapid flashes are taking place through the tube, owing presumably to the persistence of the space-charge round the cathode\*.

Indeed, when the value of the capacity across the discharge-tube electrodes is such as to give (when a telephone is included in the circuit) notes of audible frequency, the note or flashing may be maintained, provided the discharge is once initiated at values of  $E$ , the charging voltage, considerably below the normal value of  $V_c$ , the upper critical voltage.

From the above facts it may be concluded that the value of the current through the discharge-tube is greater when

\* The authors are aware that the time for the space-charge to establish or disestablish itself is of the order of  $10^{-6}$  sec. in a pure gas. But it is to be observed that when very rapid flashes are taking place, the current will never be of zero value at any instant of the extremely short "dark" period, for there is the ordinary Townsend current, due to the ionization by collision from the residual ions, which finally builds up into the glow discharge (*e.g.* see E. Reiche, *Ann. der Physik*, F. 4, B. 52, 1917). Persistence of the space-charge is used here simply to indicate the presence of residual ionization in the gas, which is the usually accepted explanation of the variation of the "sparking" potentials in gases.

large capacities are used than in the case of small capacities. This is supported experimentally by the fact that the flashes are much brighter for large than for moderately small capacities. Consequently a greater lag and variation of the going-out voltage from the normal is to be expected in the case of large capacities than in the case of the small ones.

When very small capacities are used (about 0.004 microfarad and less) the flashes are of very feeble brightness; the extinction voltage it is to be expected, therefore, will differ little, if at all, from the normal value.

*The Variation of the Current Function  $\psi(V_b')$   
with Capacity.*

In a general way it is to be expected, since the energy transferred across the tube in the luminous period decreases with decrease of the capacity across the electrodes, that the current function will decrease with  $C$  as the energy transference becomes less. Considering equation (5),

$$R_c = \frac{E - V_b'}{\psi(V_b')},$$

since  $V_b'$  decreases as the capacity  $C$  becomes less,  $R_c$  will increase with decrease of  $C$ . Now the variation of  $V_b'$  is not in most experiments of a great order, for, as will be shown later, the  $E$ ,  $R_c$  graphs do not intercept the axis of voltage at points very far removed from the normal lower critical voltage  $V_b$ ; consequently  $R_c$  may be expected to increase slowly with diminution of  $C$ .

This is what actually happens in practice (see the graphs of fig. 6) down to capacities of about 0.004 microfarad; from this point, however, the critical resistance function begins to increase rapidly, due presumably to the very small energy transference possible during the luminous period. This, of course, makes the effective resistance of the tube high, and correspondingly decreases the value of the current function  $\psi(V_b')$ .

THE EXPERIMENTAL RELATIONS.

*The Critical Resistance Relations for Large Capacities  
of the order of 1 microfarad.*

Tables I. and II. and the graphs of figs. 2 and 3 show the results obtained in the case of a capacity of approximately 1 microfarad for the  $E$ ,  $R_c$  functions over a wide range of pressures.

TABLE I.

Molybdenum-wire electrode discharge-tube.

Length of electrodes = 3.4 cm. Distance apart = 0.8 cm.

No.	P. Pressure. in mm.	$V_b'$ . Inter- cept.	$V_b$ . mean.	$i_c$ . microamps. mean.	Slope of graph.	Diam. —glow. cm.	Anode glow.
(1)...	4.06	350	315	1170	1090	0.25	{ Little at top of electrode.
(2)...	3.28	306	310	935	949	0.275	Do.
(3)...	2.68	350	317	982	875	0.4	{ Faint on part of electrode.
(4) ..	2.4	290	315	984	750	0.45	Do.
(5)...	2.16	380	315	987	733	0.55	Glow.
(6)...	1.74	315	314	618	595	0.6	Even glow.
(7)...	1.46— 1.49	315	307	518	503	0.7	Do.
(8)...	1.22	302	299	436	433	0.775	None.
(9)...	1.01	300	292	330	324	0.9	None.
(10)...	0.87	280	290	278	290	1.15	None.
(11)...	0.86	275	292	252	265	1.15	None.
(12)...	0.75	270	292	198	210	1.4	None.
(13)...	0.65	285	293	167	174	1.5	None.

Value of Capacity across the tube terminals = 0.977 microfarad.

Fig. 2.—Graphs showing the Relationship between the Charging Voltage  $E$  and the Critical Resistance  $R_c$  for a Capacity of 1 microfarad, at various Pressures.

Molybdenum-wire electrode discharge-tube.

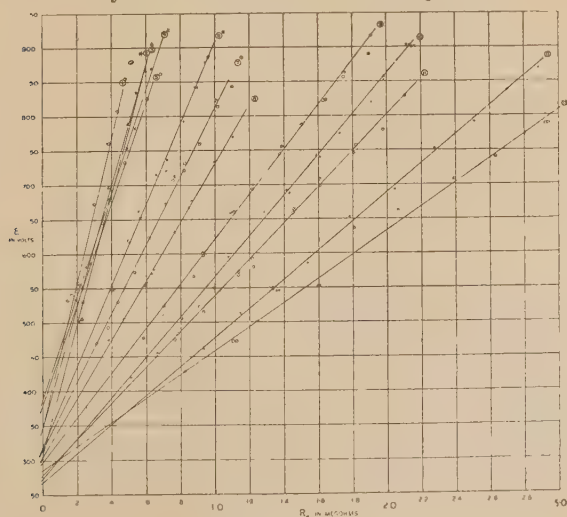


TABLE II.

## Platinum-wire electrode discharge-tube.

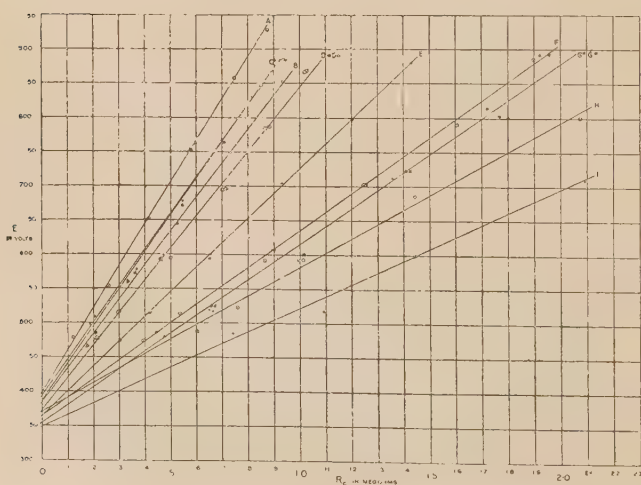
Length of electrodes = 2.5 cm. Distance apart = 0.65 cm.

No.	P. Pressure in. mm.	$V_b'$ . Inter- cept.	$V_b$ . mean.	$i_b$ . microamps. mean.	Slope of graph.	Diam. - glow. cm.	Anode glow.
(A) ...	2.58	400	382	614	612	0.45	{ Almost full electrode; bright. Do.
(B) ...	2.18	385	382	499	498	0.5	
(C) ...	2.17	394	368	573	523	0.45	Glow.
(C') ...		388		569	534	Do.	Do.
(D) ...	1.87	373	373	490	474	0.55	Do.
(D') ...	Do.	Do.	372	490	Do.	Do.	Do.
(E) ...	1.43	365	366	363	363	0.75	Do.
(F) ...	1.175	365	366	275	270	0.85	All. Velvety.
(G) ...				246			
(G') ...	1.04	355	368	253	261	0.95	Do.
(H) ...	0.94	370	370	215	211	?	?
(I) ...	0.82	348	368	165	174	Fills inter- space.	Full.

Value of Capacity across the tube terminals = 0.977 microfarad.

Fig. 3.—Graphs showing the Relationship between the Charging Voltage  $E$  and the Critical Resistance  $R_c$  for a Capacity of 1 microfarad, at various Pressures.

## Platinum-wire electrode discharge-tube.





The tube used in the experiments of which the data are given in Table I., was a molybdenum wire electrode discharge-tube, and that for Table II. a platinum wire electrode tube. The dimensions of both tubes are recorded in the tables.

Unfortunately it was not found possible to investigate the variation of  $R_c$  with capacity when the latter was more than about 1 microfarad, owing to the lack of suitable capacities. The upper critical voltage for these tubes is between four and five hundred volts, and the condensers used must, of course, be able to withstand this voltage without leakage, or the results are unreliable. It was found, however, that so far as could be ascertained, the variation of  $R_c$  was not more than a few per cent for capacities of from 0.5 to 4 microfarads.

A few general remarks relative to the experimental results may be introduced. When a tube which has been overrun is employed, it is found to be in a fairly stable condition; but notwithstanding, progressive variations of the constants of the tube occur, and the lower critical voltage especially is subject to variations.

If a tube is run for a considerable time at the critical resistance, there is a general tendency for the value of this latter to decrease; for the heating and "fatigue" effects result in an increase of  $V_a$  the cathode fall of potential (consequently increase of  $V_b$ ), and increase of the conductance of the lamp\*.

As will be seen from equations (1) and (5), these changes result in a decrease of  $R_c$ , the critical resistance. When, however, the tube has settled down to the particular conditions, the variations of  $R_c$  are not very grave.

A consideration of Tables I. and II. and the graphs of figs. 2 and 3 for the two discharge-tubes gives rise to the following general results:—

(1) The critical resistance functions are, for all the experimental pressures, linear within the limits of experimental error.

(2)

(a) In the case of the platinum-wire tube, the graphs of pressures 2.58, 2.17 mm. [(A), (c), and (c')] definitely intercept the voltage axis at a value greater than  $V_b$ , the lower critical voltage. The graph of 2.18 mm. (B), however, intercepts at  $V_b$ .

(b) In the case of the molybdenum-wire discharge-tube, the graphs of pressures 4.06, 2.68, 2.4, 2.16 mm. [(1), (3), (4), and (5)] definitely intercept at a value greater than  $V_b$ .

\* Cf. Schaufelberger, *Ann. der Phys.* (4), lxxiii. No.  $\frac{1}{2}$  (1924).

(3)

(a) The graphs of pressures 2.18, 1.87, 1.43, 1.175, 0.94 mm. [(B), (D), (E), (F), and (H)] intercept at the value  $V_b$ .

(b) The graphs of pressures 3.28, 1.74, 1.22, 1.01 mm. [(2), (6), (8), and (9)] intercept at  $V_b$ ; graph (7) of pressure 1.46 to 1.49 intercepts at a value rather greater than  $V_b$ , but there was a slight leak in the apparatus in this case.

(4)

(a) The graphs of pressures 1.04, 0.82 mm. [(G), (I)] have intercepts less than  $V_b$ .

(b) The graphs of pressures 0.86, 0.87, 0.75, 0.65 mm. [(11), (10), (12), and (13)] intercept at values less than  $V_b$ .

(5) On the average, where the intercept is greater than  $V_b$ , the slope of the critical resistance graph is less in value than the current reading  $R_c$ .

Where the voltage intercept is of the value  $V_b$ , the slope of the graph is of the same value as the current at the critical resistance.

Finally, where the voltage intercept is less than  $V_b$ , the slope of the graph is less in value than the current at  $R_c$ .

Considering the equation (5), we see that the current at the end of the flash, just before the discontinuous change from "flashing" to steady conditions, is given by

$$i' = \frac{E - V_b'}{R_c},$$

and when the conditions have become steady, the current is given by

$$i = \frac{E - V_b}{R},$$

so that evidently  $i' < i$  if  $V_b' > V_b$ ; that is to say, the slope of the  $E, R_c$  graphs,  $\frac{dE}{dR_c} = \psi(V_b') = i'$ , is less than the steady current at the critical resistance.

Further, we have  $i' = i$  if  $V_b' = V_b$ , and the slope of the graph will be of the same value as the steady current at  $R_c$ ; and finally, if  $V_b' < V_b$ ,  $i' > i$ , and the slope of the graph is of greater value than the current at the critical resistance.

It is at once evident that the foregoing experimental results agree substantially with the predictions based upon the above considerations of the critical resistance function of equation (5).

(6) It is noticeable, from a consideration of the tables, that, in a general way, at the higher pressures used, about 2 mm. and above, the voltage intercept is greater than  $V_b$ ; at the medium pressures, 1 to 2 mm. (approx.), the intercept is of the value  $V_b$ ; and at lower pressures, on the average, the intercept is less than the lower critical voltage  $V_b$ .

The experiments were, of necessity, not carried out all in one day for the different pressures, and this partly accounts for the changes in the discharge-tube constants, where the pressure is approximately the same. The sole large variation is found in the case of (C) and (C') in Table II. for the platinum electrode tube. These results were taken prior to the others, on a different day, and diverge from those of (B). The value of  $V_b$  is usually lower, however, initially, than the final value attained after the tube has settled down to the working conditions.

*Note on the Pressure-range over which "Flashes"  
may be obtained.*

In the case of the platinum wire electrode discharge-tube, flashing was obtained down to a pressure of 0.07 mm., with a charging voltage of approximately 950 volts. The negative glow under these circumstances was very diffuse, and almost filled the bulb of the discharge-tube.

There does not appear to be any definite upper limit to the pressure at which flashes may be obtained, apart from the limit imposed by the voltage available.

*The Critical Resistance Relations for Small Capacities,  
of the order of  $10^{-1}$  microfarad.*

A series of the E,  $R_c$  graphs were taken, over a range of pressures, for small capacities of the order of  $10^{-1}$  microfarad.

Table III. and the graphs of fig. 4 give the results in the case of the molybdenum-wire electrode discharge-tube for a capacity of 0.016 microfarad, over a range of pressures; Table IV. and the graphs of fig. 5 give the similar results for a capacity of 0.00875 microfarad.

A consideration of the tables and the graphs gives, as in the case of the larger capacities, the following general results:—

(1) The functions are all, within the limits of experimental error, linear.

(2) All the voltage intercepts of the graphs are of greater value than the lower critical voltage  $V_b$ , except in the case of graph IV. of Table IV., where the intercept is equal to  $V_b$ .

TABLE III.

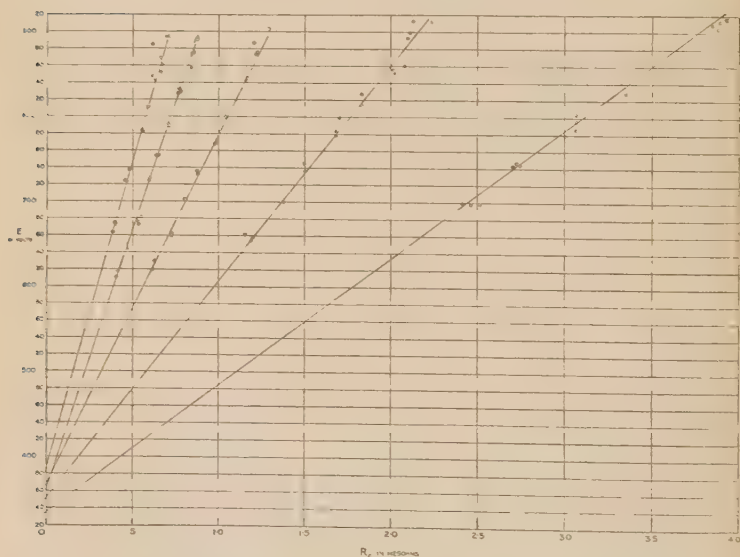
## Molybdenum-wire electrode discharge-tube.

No.	P. Pressure in mm.	$V_b'$ . Inter- cept.	$V_b$ . mean.	$i_c$ . micro- amps. mean.	Slope of graph.	$V_e$ , av. voltage before current becomes steady. mean.
(a)...	2.52	390	349	816	710	408
( $\beta$ ).....	2.0	360	345	652	603	396
( $\gamma$ ).....	1.49	350	333	450	430	380
( $\delta$ ).....	1.08	347	329	282	258	?
( $\epsilon$ ).....	0.67	336	330	164	150	?

Value of Capacity across the tube terminals = 0.016 microfarad.

Fig. 4.—Graphs showing the Relationship between the Charging Voltage  $E$  and the Critical Resistance  $R_c$  for a Capacity of 0.016 microfarad, at various Pressures.

## Molybdenum-wire electrode discharge-tube.



The intercept has in all cases a value between  $V_b$ , the lower critical voltage, and  $V_e$ , the average voltage across the tube terminals just before steadiness of the discharge ensues (see later, in section on the variation of  $R_c$ ,  $V_b$ , etc. with  $C$ ), and approaches nearer to the value  $V_b$  as the pressure is reduced.



TABLE IV.

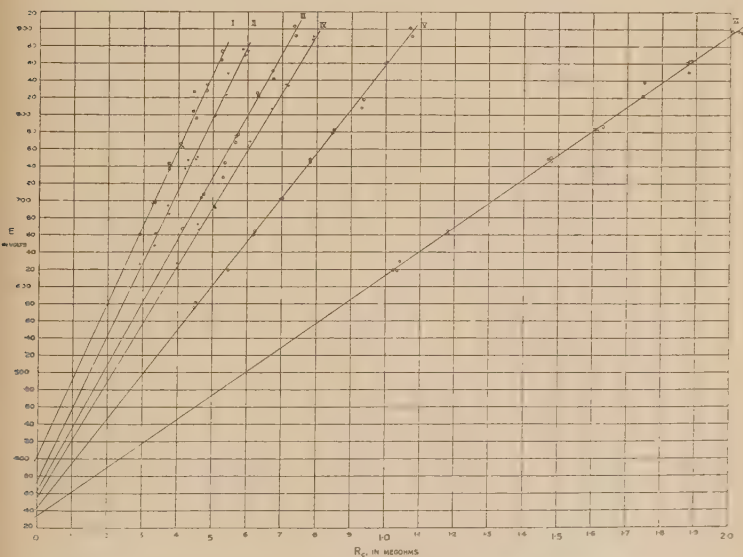
## Molybdenum-wire electrode discharge-tube.

No.	P. Pressure, in mm.	$V_b'$ . Inter- cept.	$V_b$ . mean.	$i_c$ . micro- amps. mean.	Slope of graph.	$V_e$ , av. voltage before current becomes steady. mean.
(I.)...	3.14	402	348	1032	888	414
(II.)...	2.75	374	357	886	842	410
(III.)...	2.37	363	346	752	726	400
(IV.)...	2.10	354	354	676	675	395
(V.)...	1.62	344	331	528	514	374
(VI.)...	1.09	334	322	289	280	365

Value of Capacity across tube terminals = 0.00875 microfarad.

Fig. 5.—Graphs showing the Relationship between the Charging Voltage and the Critical Resistance  $R_c$  for a Capacity of 0.0085 microfarad, at various Pressures.

Molybdenum-wire electrode discharge-tube.



(3) Where the voltage intercept of the graph is greater than  $V_b$ , as is to be expected, the slope of the graph  $\left(\frac{dE}{dR_c}\right)$  is less in value than the steady current reading at the critical resistance  $R_c$ .

In the case of graph IV. of fig. 5, where  $V_b'$ , the voltage intercept, is equal to  $V_b$ ,  $i'$  the slope of the graph is equal in value to  $i$  the current at the critical resistance.

It will be noticed that there has been a considerable change in the value of  $V_b$ , between the obtaining of the results for the 1 microfarad capacity, and the above results.

*The Variation of  $R_c$ ,  $V_b$ , etc. with  $C$ .*

The variation of the critical resistance  $R_c$  with the capacity was investigated at two different pressures for the molybdenum-wire electrode discharge-tube. Table V. and the graphs of fig. 6 show the variations.

With large capacities the critical resistance increased gradually with diminution of  $C$ , but when the capacity became of the order of 0.004 microfarad and less, the value of  $R_c$  began to increase rapidly with decrease of  $C$ , and in the case where the voltmeter alone was across the lamp terminals, attained several times the value for large capacities.

The voltage across the lamp electrodes at the point where the discharge changes discontinuously from the flashing to the steady state was observed together with the current, as given by a unipivotal galvanometer, for this critical point. As the discharge under these conditions is periodic in character, it is apparent that the voltage reading  $V_e$  is the average voltage over the complete cycle of the condenser charging and discharging between the upper and lower critical voltages. These measurements are given in Table V.

It is noticeable that when the circuit resistance is somewhat greater than the critical resistance value, the voltage across the lamp terminals, when small capacities are used, remains constant for a considerable range of resistance as  $R$  is decreased. We would conclude from this constancy that  $V_e$  represents the limiting average voltage over the whole cycle, when the luminous period becomes great in comparison with the "dark" period.

The practically obtained value is not sufficiently constant to compare directly with that derived theoretically; moreover, the variations of  $V_b$  and  $V_e$  with  $C$  inhibit any comparison based on the normal values of these voltages.

$V_e$ , as is to be expected, decreases with decrease of  $C$ , for both  $V_c$  and  $V_b$  become less in magnitude, and consequently the average voltage over the whole cycle between  $V_c$  and  $V_b$  (that is  $V_e$ ) will decrease with decrease of the capacity.

The current reading  $i_e$  is similarly the average current over the total period, whilst  $i$ , given in Table V., is the current value when the discharge becomes truly steady.

TABLE V.

C. microfarads.	$V_e$ mean.	$V_b$ mean.	$R_c$ mean.	$i$ microamps. mean.	$i$ microamps. mean.
0.977	—	314	0.47	—	541
0.063	380	316	0.53	336	475
0.055	377	316	0.535	334	469
0.066	375	316	0.56	323	456
0.031	377	317	0.565	306	445
0.016	372	314	0.57	348	448
0.0088	367	316	0.57	350	446
0.0041	357	317	0.595	352	426
0.0023	329	317	0.63	338	402
0.0012	332	316	0.69	314	351
0.0004	326	315	0.89	240	274
0.00007	324	315	1.13	198	208
Voltmeter alone.					

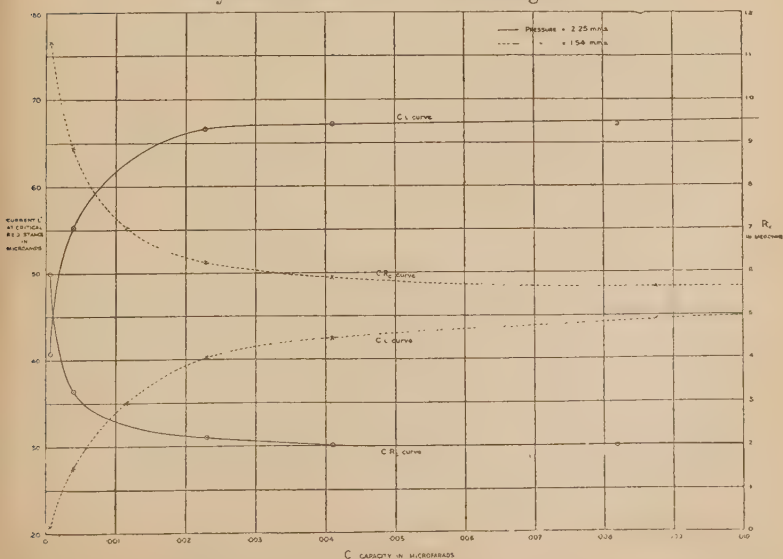
Pressure of air in tube = 1.45 mm.

0.977	—	326	0.978	—	832
0.055	414?	327	0.13	528	752
0.032	395.5	327	0.153	568	716
0.015	386	328	0.182	564	694
0.0082	383	324	0.202	556	672
0.0041	382	326	0.207	568	674
0.0023	376	327	0.223	580	668
0.0004	362	328	0.33	510	554
0.00007	348	325.5	0.6	356	408
Voltmeter alone.					

Pressure of air in tube = 2.25 mm.

Fig. 6.—Graphs showing the Variation of the Critical Resistance  $R_c$  with the Capacity C for two different Pressures.

Molybdenum-wire electrode discharge-tube.



Both  $i_c$  and  $i$  decrease with decrease of the capacity across the lamp electrodes. With large capacities the diminution with  $C$  is very slow down to a point at a capacity of about 0.004 microfarad (the same point at which  $R_c$  begins to increase rapidly), where a very rapid diminution of these quantities, as  $C$  is made less, sets in.

When the discharge has attained a steady state, the tube of course adjusts itself to carry the maximum current possible under the existing conditions—that is, the voltage across the lamp terminals drops to the lowest possible value,  $V_b$ . This voltage as well as the current  $i$  was measured.  $V_b$ , as is shown in the table, is found within the limits of experimental error to be independent of the capacity  $C$ .

### *The Variation of the Effective Lower Critical Voltage $V_b'$ .*

It has been shown in the case of the "Osglim" lamp that the going-out or extinction voltage (lower critical voltage) is of greater value than normal when *sudden reduction* of the current in the circuit is made by reduction of the voltage across the lamp terminals\*. The present authors have observed a similar phenomenon in the air discharge-tubes used in these experiments. Mr. Tarrant, in his contribution to the discussion on a previous paper on the critical resistances for the "Osglim" lamps, states that the lower critical voltage for the lamp is not constant if large charges are passed through the lamp during the luminous period†. "Under these conditions the extinction voltage for the lamp was considerably higher than that measured when the lamp was running in a steady state, or when a small parallel capacity only was used"‡.

One of us, in recent preliminary experiments on the variation of the lower critical voltage with the capacity across the lamp and the energy thrown through during the luminous period, has observed similar variations, though not so great as those observed by Mr. Tarrant (the lamps were aged by

\* Shaxby and Evans, Proc. Phys. Soc. Lond. xxxiv. pt. 4, p. 280.

† It may be pointed out here that in the experiments on the critical resistance of the "Osglim" lamps, previously referred to, the conditions were such (since resistances were included in the condenser circuit so that a part only of the cathode was employed in discharge, and variations were made gradually) that  $V_b'$  corresponded, within the limits of experimental error, to the normal lower critical voltage  $V_b$ .

‡ See Proc. Phys. Soc. Lond. xxxiv. pt. 4. Discussion (Mr. A. G. Tarrant), p. 280.

overrunning). It appears that similar results hold in the case of the air discharge-tube.

The experimental results are then, at least qualitatively, in agreement with those predicted in the theoretical section of the present paper. They certainly confirm the fact of the divergence of the effective lower critical voltage  $V_b'$  from the normal  $V_b$ , in the case of the 1 microfarad capacity, at pressures above 2 mm., and in the case of the small capacities over a much wider range. Unfortunately, the results obtained above, for the divergence of  $V_b'$  from  $V_b$ , do not lend themselves to any quantitative codification. In a general way it has been demonstrated, by taking graphs for many small capacities, that the voltage intercept, in agreement with the deductions made in the theoretical section on the variation of  $V_b'$ , approaches nearer to the normal value  $V_b$  as the capacity across the lamp is made less. The results obtained are not sufficiently consistent for the authors to make any final claims in the matter.

Certain results seem to indicate that the erratic values obtained for  $V_b'$ , even at the same pressure, may be intimately connected with the appearance and disappearance of the anode glow.

Experiments carried out to determine whether there was any connexion between the types of the discharge and the values of  $V_b'$  were inconclusive. The sole general rule that is apparent is for the tubes with large capacities across them. Where there is an anode glow, the value of  $V_b'$  is either greater than or equal to that of  $V_b$ , and where there is no anode glow,  $V_b'$  is either less than or equal to  $V_b$ .

In conclusion, we wish to acknowledge our indebtedness to Prof. G. W. Todd, of Armstrong College, under whose supervision the experiments were carried out, and to the Department of Scientific and Industrial Research for the grant which has enabled one of us to undertake the work.

Armstrong College,  
Newcastle-upon-Tyne.



XXXVII. *Chemical Affinity and Electronic Structure.*—  
 Part I. *The Non-polar Bond.* By BERNARD HOWELL  
 WILSDON\*.

THE recent great advances in our knowledge of the constitution of the atom have resulted in various attempts to construct a theory which will explain the main facts of chemistry included under the name affinity. So far, these have been of only a qualitative or descriptive nature. While they enable systems of chemical notation, more or less complicated, to be expressed in terms of electrons, which may aid the chemist in visualizing the chemical bond, it is scarcely to be expected that they will afford a basis for a quantitative theory unless the mechanism postulated corresponds with physical realities. For this reason a static model molecule, such as that associated with the names of Lewis and Langmuir, cannot long meet all the requirements of a theory of chemical combination.

In what follows is given an outline of a theory which it is believed will at least provide a basis for the discussion of chemical combination in a manner consistent with our present knowledge of the atom. It has the further merit of being quantitative; besides affording a method of attacking the energetics of reactions, it also gives some insight into the geometrical structure of the molecule.

The fundamental assumption on which the theory rests is that, in order that the free valency orbits of uncombined atoms shall be capable of forming a chemical link or bond, they must have identical or harmonically related frequencies (see Note at end of paper). Change in the frequency of an electronic orbit, without a jump of the principal quantum number, may be brought about either by the precessional rotations which result from the action of a magnetic field, or by the nutational movements impressed by an electrostatic field. Conversely, we may legitimately regard a change in the natural frequency of an orbit which takes place without the large energy change involved in a jump of the principal quantum number, as *producing* a magnetic or electrostatic field. The accommodation in frequency which we assume to be necessary in order that two discordant orbits shall unite to form a chemical bond, may therefore be supposed to be quantitatively related to the field of force which binds two atoms. Bonding brought about by a magnetic field will obviously correspond with a

\* Communicated by Dr. J. W. Nicholson, F.R.S.

non-polar type of combination ; an electrostatic origin will then give rise to the polar bond.

A change in frequency of an orbit represents only a change in kinetic energy. Associated with this there will be a change in potential energy. In the case of an electrostatic field it is known that the kinetic energy of an orbital electron bears always a constant ratio to the potential energy. This result was due originally to Bohr (Phil. Mag. xxvi. p. 24, 1913), who states: "In every system of nuclei at rest and electrons which move in circles with velocities which are small compared with the velocity of light, the kinetic energy except in sign, is equal to half the potential energy." Sommerfeld (*cf.* 'Spectral Lines and Atomic Structure,' Eng. Trans. p. 447) has generalized this theorem, which he shows is not limited to circular orbits when time mean values are considered. The Coulomb field may also be replaced by any other in which a definite law of force holds. Under these conditions it is shown that if the potential energy of the field is a homogeneous function of degree  $n+1$  of the coordinates of position, in general, the time mean values of the kinetic and potential energies will be related as follows :

$$E_{\text{kin.}} = \frac{n+1}{2} E_{\text{pot.}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the case of a non-polar bond, since the magnetic moments of the orbits are quantized, we may represent dimensionally the work done in breaking the bond by an equation of the form

$$-W = \frac{\Sigma \mu_1 \mu_2}{r^3},$$

where  $\Sigma \mu_1 \mu_2$  represents the scalar product of the magnetic moments and  $r$  is some linear coordinate. The law of force will therefore be given by

$$\frac{\partial W}{\partial r} = F = \frac{3 \Sigma \mu_1 \mu_2}{r^4},$$

whence  $n$  in equation (1) is equal to  $-4$  ; substituting in (1) we have

$$E_{\text{kin.}} = -\frac{3}{2} E_{\text{pot.}} ;$$

consequently

$$Q = \Delta E_{\text{kin.}} + \Delta E_{\text{pot.}} = \frac{1}{3} \Delta E_{\text{kin.}}, \quad . \quad . \quad . \quad (2)$$

where  $Q$  is the total energy change.

As our assumption regarding the tuning of free orbital frequencies enables us to estimate the change in kinetic energy from a knowledge of the natural frequencies of the orbits of uncombined atoms, it should be possible, under conditions which will be described later, to make use of the above relation between the kinetic and potential energies of orbits in a magnetic field to calculate the heats of formation of non-polar compounds. It will be shown below that heats of formation can be calculated which agree well with those observed for simple compounds, using only theoretical values for the frequencies of atoms in their ground orbits and without the use of arbitrary quantum numbers.

*The available energy of bond formation.*—When similar atoms combine, if both valency electrons are in their ground orbits, their frequencies will be the same and there will consequently be no energy available by accommodation in frequency, to provide the energy of the bond. This is not the case in the union of dissimilar atoms: here, the accommodation in the frequencies of the naturally discordant ground orbits is capable of providing the bond energy. We may infer, therefore, that it is only in the combination of similar atoms that activation is a necessary preliminary to reaction. This does not of course preclude the possibility that activation may also occur in other types of combination.

The energy of activation does not enter into the balance sheet which represents an ordinary thermochemical reaction: otherwise, the reaction which takes place when hydrogen atoms combine to form the hydrogen molecule should be endothermic, which is not the case. On decomposition of such a molecule the energy required will be that necessary to re-form one activated and one unactivated atom. If the activated atom then resumes its ground orbit the light quantum emitted will not be recorded as a heat change.

We therefore suppose the energy available for bond formation is given by

$$h(\nu_1 - \nu_2), \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $\nu_1$  and  $\nu_2$  represent, either the natural frequencies of two dissimilar atoms, or the frequencies of similar atoms at two different energy levels. The difference of the two terms then corresponds with the energy of emission of a spectral line. In what follows, the natural frequencies  $\nu_1$  and  $\nu_2$  are calculated from the formula

$$\nu = R_0 \frac{Z_e^2}{n^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here  $R_0$  is the Rydberg constant,  $Z_e$  is the effective atomic number and is equal to the number of electrons in the valency shell minus the screening number of Sommerfeld;  $n$  is the principal quantum number of the orbit. Values for  $s_p$ , the screening number, and  $Z_e^2$  for different numbers of valency electrons  $p$ , are given for reference in Table I. These numbers correspond with vertical columns of the periodic table of the same number as  $p$ .

TABLE I.

$p$ .	$s_p$ .	$Z_e^2$ .
1 .....	0.000	1.000
2 .....	0.250	3.061
3 .....	0.577	5.862
4 .....	0.957	9.249
5 .....	1.377	13.13
6 ..	1.828	17.40
7 .....	2.305	22.05

From (4), if  $E_a$  represents the available bond energy per gram molecule, we have

$$E_a = \frac{hR_0}{J} L \left( \frac{Z_{e_1}^2}{n_1^2} - \frac{Z_{e_2}^2}{n_2^2} \right), \quad . \quad . \quad . \quad (5)$$

where  $L$  is Avogadro's number and  $J$  is the mechanical equivalent of heat. The factor,  $A = \frac{hR_0}{J}$ , becomes on substituting the values,  $R=109721.6 \text{ sec.}^{-1}$ ,  $h=6.55 \times 10^{-27} \text{ erg secs.}$ ,  $L=0.606 \times 10^{24}$ , and  $J=4.187 \times 10^7 \text{ erg/cal.}$ ,

$A = 310.2$  kilogram calories per gram molecule.

*Calculation of the change in kinetic energy on bond formation.*— $E_a$ , the available bond energy, will only represent the change in kinetic energy on combination under certain conditions. If energy is used in distorting the constituent elements of structure of the molecule, the change in kinetic energy must necessarily be less than the available energy calculated from (5). The distribution of energy in the molecule may then be expected to correspond with what takes place in the anomalous Zeeman effect in the magnetic resolution of spectral lines. The change in kinetic energy will thus be affected by a factor similar to the Runge denominator. The normal or Lorentz resolution, represented by  $\Delta\nu_{\text{norm.}}$ , only occurs when the impulse taken up

by the electronic orbits does not affect other orbits or the molecular trunk. It is, however, this "normal resolution" representing purely kinetic energy which it is our object to calculate. If all the available bond energy were retained in kinetic form in the molecule,  $h\Delta\nu_{\text{norm.}} = E_a$  would give the work which would be done in restoring the original frequencies of the electronic orbits in each atom, *i.e.* the Runge denominator is equal to unity. By (2) one-third of this amount would represent the total energy change and would thus give the heat of decomposition of the molecule.

In order to calculate the distribution of the available bond energy in the molecule, we may make assumptions similar to those of Landé (*Zeitschr. f. Phys.* 1921, p. 231) in the calculation of the anomalous Zeeman effect. The hypothesis is adopted that the distribution of impulse depends on changes by half units in the azimuthal quantum numbers of the orbits. The impulses corresponding with these changes may affect both electronic orbits and molecular trunk. We may calculate the energy of the molecule on the supposition that the orbits in one half are affected by an external magnetic field originating from the second half. By symmetry the total energy will then be given by twice this amount, since the action of both halves of the molecule must be reciprocal. Following the method of spatial quantizing developed by Sommerfeld, we may also assume that besides the quantum restriction to changes in the moments of orbits, connected with change in their azimuthal quantum numbers, also their components in the molecular field can only attain discrete values. This assumption gives a relation determining the orientation of orbits in the molecule.

In the simplest cases, where the trunk is incapable of acquiring magnetic moment, or where the impulses to which it is subjected are of opposite sign, the whole available energy of the bond will be confined to the interaction between orbits and field. If  $k$  represents the azimuthal quantum number of the free valency orbit, we assume that it changes, under the influence of the field of the second atom, to  $k - \frac{1}{2}$ . If the trunk remains unaffected, the energy of the orbit in the field of the second atom will be given by

$$(k - \frac{1}{2})BH \cos \theta, \dots \dots \dots (6)$$

where  $B$  is the unit of magnetic moment of Bohr, and is equal to  $eh/4\pi mc$ ,  $e$  being the charge of an electron,  $h$  the Planck unit of action,  $m$  the mass of the electron, and  $c$  the velocity of light.  $H$  is the field strength of the second



atom, and  $\theta$  the angle made by the vector normal to the orbit with the direction of H. Lorentz's equation for the normal resolution of spectral lines in a magnetic field is

$$\Delta\nu_{\text{norm.}} = \frac{eH}{4\pi mc} \dots \dots \dots (7)$$

Substituting in (6) we have, including the symmetry factor 2,

$$E_a = 2[(k - \frac{1}{2}) \cos \theta] h \Delta\nu_{\text{norm.}}, \dots \dots (8)$$

The possible values of  $\cos \theta$  are given by combinations of  $\frac{l_1}{l_1 + l_2}$ , where  $l_1$  and  $l_2$  are Sommerfeld's equatorial and latitudinal quantum numbers whose sum  $l_1 + l_2$  (usually denoted by  $n_1 + n_2$ ) is equal to  $k$  the azimuthal quantum number.

In the case of hydrogen where  $k$  changes to  $(1 - \frac{1}{2})$  the only possible values of  $\cos \theta$  are 0 and 1.  $\cos \theta$  must therefore be equal to 1, i.e. the orbit adjusts itself at right angles to the direction of the field of the second atom. Substituting for E from (5) we have

$$E_a = A \left( \frac{Z_{e_1}^2}{n_1^2} - \frac{Z_{e_2}^2}{n_2^2} \right) = 2(k - \frac{1}{2}) \cos \theta \cdot h \Delta\nu_{\text{norm.}},$$

whence

$$\Delta\nu_{\text{norm.}} = A \left( \frac{Z_{e_1}^2}{n_1^2} - \frac{Z_{e_2}^2}{n_2^2} \right) \cdot \frac{1}{2(k - \frac{1}{2}) \cos \theta}.$$

Q will then be given by

$$Q = \frac{1}{3} h \Delta\nu_{\text{norm.}} = \frac{A}{3} \left( \frac{Z_{e_1}^2}{n_1^2} - \frac{Z_{e_2}^2}{n_2^2} \right) \cdot \frac{1}{2(k - \frac{1}{2}) \cos \theta}. \quad (9)$$

For the hydrogen molecule we thus obtain, since  $Z_e^2 = 1$ ,  $n_1 = 1$ ,  $n_2 = 2$ ,  $\cos \theta = 1$ ,

$$Q = \frac{310 \cdot 2}{3} \left[ \frac{1}{1} - \frac{1}{4} \right] \cdot \frac{1}{1} = 77 \cdot 55 \text{ Cal.}$$

This compares favourably with the experimental value of 85 calculated by Langmuir and the value of 81 found by Frank and Knipping (*Ber. Deut. Phys. Gesch.* xxi. p. 738, 1919). The calculated value is within the probable experimental value of the determinations.

With the halogen elements the outer valency electron has a value of  $k = 2$ , which changes to  $(2 - \frac{1}{2})$  in the molecular magnetic field. The heats of dissociation will then be given, since  $Z_e^2 = 22 \cdot 05$ , with  $\cos \theta = 1$ , by

$$Q = \frac{310 \cdot 2}{3} \cdot 22 \cdot 05 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \cdot \frac{1}{2[2 - \frac{1}{2}]} \cdot 1.$$

Table II. gives all the data required for the calculation of the heats of dissociation together with the theoretical and observed values. The latter are taken from Landolt and Börnstein's Tables (edn. 4) unless otherwise stated.

TABLE II.

Heats of dissociation of monovalent gaseous elements.

Element.	$Z_e^2$ .	$n_1$ .	$n_2$ .	$k$ .	$\cos \theta$ .	Q calc.	Q found.
H .....	1	1	2	1	1	77.55	81.85
F .....	22.05	2	3	2	1	316.5	• ?
Cl .....	„	3	4	2	1	110.6	113.0
Br .....	„	4	5	2	1	51.3	55.3
I .....	„	5	6	2	1	27.9	36.86

The agreement is sufficiently remarkable, considering the errors involved in practical measurements, to warrant the feeling that the theory is on sure ground. All the values appear to be low, divergencies increasing with the molecular weight, as might be expected. Of the possible values of  $\cos \theta$  we have selected the value 1; arbitrariness may be avoided, however, by adopting a provisional hypothesis which is applied consistently in what follows. This is that the components of moment of momentum of all *active* valency orbits in the direction of the field of the second atom, or other half of the molecule, shall be equal to the moment of the bond electron. This is expressed in the formula

$$(k - \frac{1}{2}) = \sum_s (k - \frac{1}{2}) \cos \theta, \quad . \quad . \quad . \quad (10)$$

where  $s$  is the number of active valency orbits. In the case of the halogen elements  $s$  is 1, so  $\cos \theta$  is also necessarily unity.

The same method, with the hypothesis expressed in (10), will now enable us to calculate the Runge denominator for more complicated molecules where the moment of the trunk may not be zero as in the cases so far discussed. The number of "active" valency electrons in an atom is in general equal to the principal valency of the element. The  $p-s$  valency electrons are assumed to lock up together with the trunk into a configuration of zero moment. With nitrogen we shall then have  $2k_1 = p-s$  and  $3k_2 = s$ ; with oxygen,  $4k_1 = p-s$ ,  $2k_2 = s$ ; with the halogens possibly  $4k_1 + 2k_2 = p-s$ ,  $1k_2 = s$ . Following Sommerfeld in his explanation of the anomalous Zeeman effect of doublet and triplet

atoms, we then suppose that the direction of the moment of the bond orbit is defined by an angle  $\theta_1$ ; the remaining  $s-1$  "active" valency orbits are considered to be associated with the trunk in such a way that the moment of the whole complex [trunk +  $(s-1)$  valency orbits] is given by the sum of the individual moments and is defined in direction by the common angle  $\theta_2$ . The moments of all active valency orbits will be affected in the same way by change in their azimuthal quantum numbers by  $\frac{1}{2}$ . A corresponding number of  $\frac{1}{2}$  units represents the gain in moment of the trunk. The total moment of the trunk will also depend on the impulses received in the other half of the molecule, which may differ in sign. Thus in the case of the halogen elements the trunk receives an impulse of  $+\frac{1}{2}$  in one half of the molecule and  $-\frac{1}{2}$  in the other; the total moment is therefore zero, as has been assumed above.

The magnetic energy of the half molecule will now be made up of three parts:—

- (1) The energy of the "outer" or bond electron in the field of the other half of the molecule. If  $\theta_1$  defines the direction made by the vector normal to this orbit with the direction of H, this energy will be equal to  $(k-\frac{1}{2})BH \cos \theta_1$ .
- (2) The energy of the inner complex in the field H. If T'B represents the moment of this complex and  $\theta_2$  the angle its direction makes with H, this energy will be represented by an amount  $T'BH \cos \theta_2$ .
- (3) The energy of strain between the inner complex and the bond electron. In magnitude the field of this electron will be equal to that of the second atom. If  $\theta$  represents the angle between the moment of the inner complex and the field of the bond electron, this energy will be  $T'BH \cos \theta$ .

Summing these amounts and substituting for H in terms of  $\Delta\nu_{\text{norm.}}$  by (7), we have

$$E_a = 2\{(k-\frac{1}{2}) \cos \theta_1 + T'(\cos \theta_2 + \cos \theta)\} \cdot h\Delta\nu_{\text{norm.}} \quad (11)$$

The resultant moment of all orbits in the direction of H must, however, be equal to that of the bond electron by (10). Thus if T represents the moment of the trunk, as distinct from that of the complex (trunk inner valency electrons), we have

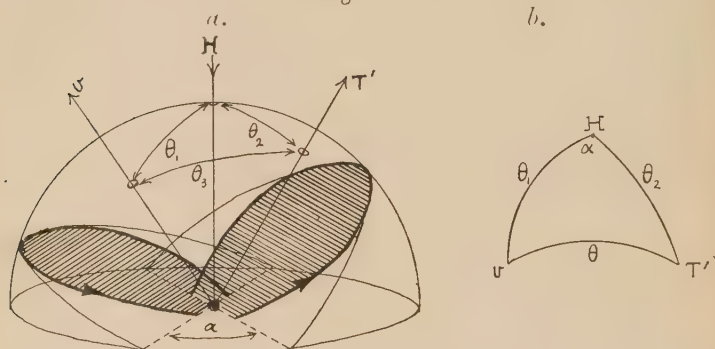
$$(T' - T) \cos \theta_2 + (k - \frac{1}{2}) \cos \theta_1 = (k - \frac{1}{2}). \quad (12)$$

(10) may now be written

$$E_a = 2\{(k - \frac{1}{2}) + T \cos \theta_2 + T' \cos \theta\} h\Delta\nu_{\text{norm.}} \quad (14)$$

A relation between the angles  $\theta$ ,  $\theta_1$  and  $\theta_2$  may now be obtained by demanding that the orbits and trunk shall be in equilibrium so that a small displacement will result in no energy change. In diagram 1,  $a$  represents the arrangements of orbits on one side of the equatorial plane of a molecule,  $b$  represents a stereographic projection of the points where the vectors concerned pierce a sphere surrounding the molecule.  $v$  represents the vector normal to the bond orbit,  $H$  the field of the second atom, and  $T'$  the inner complex.

Fig. 1.



The angles of the spherical triangle will then be related as follows:

$$\cos \theta = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \alpha. \quad (15)$$

Substituting for  $\cos \theta$  in (14), we have

$$E_a = 2\left\{(k - \frac{1}{2}) + T \cos \theta_2 + T' (\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \alpha)\right\} h \Delta \nu_{\text{norm.}} \quad (16)$$

The conditions for equilibrium of orbits and trunk may be written

$$\frac{\partial E_a}{\partial \theta_2} = \frac{\partial E_a}{\partial \alpha} = 0. \quad (17)$$

This requires that  $\cos \alpha = 1$ , and gives the following relation between the angles  $\theta_1$  and  $\theta_2$ ,

$$\tan \theta_2 = \frac{T' \sin \theta_1}{T + T' \cos \theta_1}. \quad (18)$$

Expressing all angles in (16) in terms of  $\theta_1$ , we have

$$\frac{E_a}{2} = \left(k - \frac{1}{2} + \sqrt{T^2 + 2TT' \cos \theta_1 + T'^2}\right) h \Delta \nu_{\text{norm.}} \quad (19)$$

As examples of the use of formula (19) we may consider first the union of the elements oxygen and nitrogen. Effectively we regard the two atoms of the molecule as linked by a single "bond" and calculate the Runge denominator by considering the moment of the inner electron and trunk. In the case of oxygen there are two active valency electrons, i. e.  $s=2$ . The moment of the trunk will then be  $\frac{1}{2} + \frac{1}{2} = 1 = T$ . Since there is one "inner" valency orbit,  $T' = 1 + 3/2$ . If we substitute the value of  $\theta_2$  of (18) in equation (10) we obtain a complicated cubic. Considering the order of accuracy attainable in the empirical results by which we shall test our theoretical deductions, it will be sufficient for the present to determine the limits between which the Runge denominator must lie. If we call the expression under the square root in (19)  $X$ , we obtain the following values for corresponding values of  $\cos \theta_1$  shown :

$\cos \theta_1$ .	$X$ .
1 .....	7/2
2/3 .....	3.258
1/3 .....	2.986
0 .....	5/2

We may legitimately reject the value for  $\cos \theta = 0$ . The heat of dissociation will then be given by

$$Q = \frac{17.4}{3} \left( \frac{1}{4} - \frac{1}{9} \right) \cdot \frac{1}{r},$$

where

$$r = 2\left(\frac{3}{2} + X\right).$$

Substituting the values of  $X$  calculated above, we obtain the values  $Q = 24.99$ ,  $26.27$ , or  $27.85$ . The experimental value is  $26.0$ , which is mid-way between our theoretical limits.

Using a precisely similar method for nitrogen where  $T = 3/2$ ,  $T' = 3/2 + 2(3/2)$ , we obtain for  $r$  :

$\cos \theta_1 = 1$	$r = 15$	$Q = 12.57$
2/3	14.23	13.25
1/3,	13.39,	14.08.

The value found is  $13.0$ ; again our theoretical values approximate closely.

So far we have confined ourselves to symmetrical compounds. In the case of the halogen hydracids we assume that the moment of the trunk becomes  $\frac{1}{2}$  due to the change



of the  $k_2$  halogen orbit, and  $-(-\frac{1}{2})$  for the hydrogen. T thus becomes unity and  $T=T'$ , since there are no other orbits free in the molecule but the bond orbit. X is 2, and  $r$  is therefore given unambiguously as  $2(3/2 + 2) = 7$ .

Table III. gives all the data for the calculation of the theoretical heats of dissociation according to the formula

$$Q = \frac{A}{3} \cdot \frac{1}{7} \left( \frac{22.05}{n_2^2} - \frac{1}{1} \right),$$

together with the experimental values.

TABLE III.

Heats of dissociation of halogen hydracids.

Acid.	$n$ .	$n$ .	$k$ .	$\cos \theta_1$ .	$r$ .	Q calc.	Q found.
HF .....	1	2	2	1	$7 \times 2$	33.3	38.5
HCl .....	1	3	2	1	7	21.4	22.0
HBr .....	1	4	2	1	7	5.43	8.6
HI .....	1	5	2	1	7	-3.5	-6.4

Except in the case of hydrofluoric acid, where it is necessary to increase the Runge denominator to twice its value, the theoretical results agree satisfactorily in magnitude and sign with experimental results. The abnormality of HF is not surprising; we may suppose the heat change represents the formation of two molecules. This tallies with the chemical evidence. It is particularly satisfactory that the sign of the reaction reverses precisely at the point where the natural frequency of the halogen becomes smaller than that of hydrogen. It is not advisable at present to advance a general rule for the determination of the sign of the heat change until more reliable data are forthcoming. It may be noted, however, that the necessity for the atom of highest valency (the "key" atom) to *diminish* in frequency under the influence of the molecular field, implies negative values in the case of  $H_2Te$ ,  $SbH_3$ , and  $Cl_2O$ , as are observed; but  $AsH_3$  and  $H_2Se$  appear to be exceptional, if the empirical figures can be relied on, which is certainly very doubtful in the case of  $AsH_3$ . The consistently negative values for unsaturated compounds are explicable in another manner and will be dealt with in a future communication.

In the case of water the moment of one OH trunk will be zero, since it receives the impulse  $+\frac{1}{2}$  from the O orbit and  $-\frac{1}{2}$  from the hydrogen. Since we are dealing with a bi-valent key atom we must take into account the second orbit.

We may reasonably assume that this will be equal to the sum of the moments of the oxygen and hydrogen orbits, *i. e.*  $3/2 - \frac{1}{2} = 1$ . We thus get  $r = 2(3/2 + 1) = 5$ . The formula

$$Q = \frac{A}{3} \cdot \frac{1}{r} \left( \frac{17.4}{4} - \frac{1}{1} \right),$$

then gives  $Q = 69.2$  Cal. The value found is 69.0.

Applying the same method to ammonia, we must recognize that the symmetry factor will no longer be two, but three, as there are three separate bonds to be considered. The nitrogen will receive  $+3(\frac{1}{2})$  from its  $3k_2$  valency orbits, the hydrogen (only one must be considered as we are calculating the energy of one bond) will contribute  $-(\frac{1}{2})$ , so  $T$  will be 2. There are two loose valency orbits each of moment  $3/2 - \frac{1}{2}$ , so  $T'$  becomes 4.  $r$  will now be  $3(3/2 \times X)$ . The following are the values of  $r$  and  $Q$  for the assumed values of  $\cos \theta_1$  :—

$\cos \theta_1 = 1$	$r = 22.5$	$Q = 10.48$
$2/3$	$21.11$	$11.17$
$1/3$	$19.59$	$12.04$

The experimental value is 11.89.

In Table IV. are given  $E_a$ , and the observed heats of formation  $Q_{\text{obs.}}$ , for the trivalent compounds shown. In the fourth column values of  $r$  are given which would reduce the theoretical value  $E_a$  to the  $Q$ 's shown in the fifth column.

TABLE IV.

Compound.	$E_a$ .	$Q$ obs.	$r$ .	$E_a/r$ .
$\text{NH}_3$ .....	235.8	11.89	20	11.79
$\text{PH}_3$ .....	47.57	4.9	10	4.8
$\text{AsH}_3$ .....	-18.55	44.2?	?	?
$\text{SbH}_3$ .....	-49.1	-33.96	$3/2$	-33.4
$\text{BF}_3$ .....	418.3	234.6	$3/2$	278
$\text{BCl}_3$ .....	101.63	89.1?	?	
$\text{PCl}_3$ .....	102.5	69.7	$3/2$	68.32

It will be noted that the value of  $r$  which it is necessary to assume in the case of  $\text{PH}_3$  is very approximately  $\frac{1}{2}$  of the theoretical value for ammonia. With other compounds on which any reliance can be placed, the value of  $r$  seems to sink to  $3/2$ . This is the value  $r$  would assume theoretically if the impulses were distributed in such a way that the

moment of the trunk were zero, and a numerator were introduced which would cancel the symmetry factor of 3. This will be referred to again when considering the phenomena of quadrivalent compounds.

With carbon we assume there are two electrons in  $k_1$ , and two in  $k_2$  orbits. If all are active this implies that the impulse received by the trunk from two of them will neutralize that received from the other two. The Runge denominator should then be simply  $4(3, 2) = 6$ . Here we assume  $T'$  is also zero, since the most symmetrical arrangement of the valency orbits which also satisfies the requirements of equation (10) is that in which there are three bonds in the  $\cos \theta = 1/3$  position on one side of the equatorial plane, and one at  $\cos \theta = 1$  on the other. Both halves of the molecule then obey the condition that the components of momentum in the direction of the field (at right angles to the equatorial plane) shall be equal to  $k - \frac{1}{2}$ . Table V. gives observed and calculated values of various quadrivalent compounds.

TABLE V.

Compound.	$E_a$ .	Q obs.	$r$ .	$q$ .	Q calc.
$\text{CH}_4$ .....	135.6	20.35	6	1	22.6
$\text{CCl}_4$ .....	42.81	21.03	6	3	21.4
$\text{SiF}_4$ .....	464.0	239.8	6	3	232.0
$\text{SiCl}_4$ .....	146.8	121.8	?	?	?

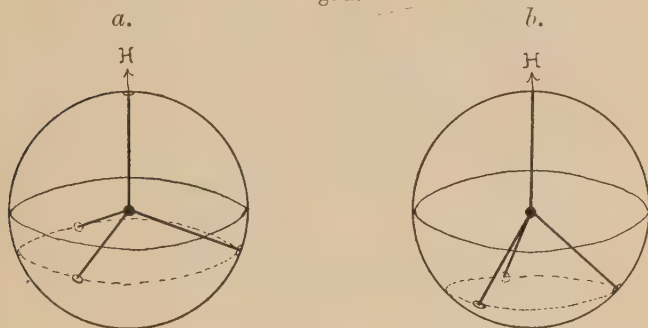
The theoretical value for  $\text{CH}_4$  agrees well; with the others the numerator, designated  $q$ , which it is necessary to assume appears to be 3. Although the numerator is purely arbitrary, the fact that for similar types of compounds it tends to reduce to the same number would indicate that the agreements then obtained are not entirely accidental. The factor  $q$  appears to be connected with the ratios of the principal quantum numbers of the linked orbits, but more cannot be said on this point till further evidence is available.

*Structural considerations.*—The fact that the disposition of orbits in the carbon atom will depend only on their mutual interactions, without interference by the moment assumed by the trunk, is apparently responsible for the characteristic chemical properties of this element. Stereoisomerism is evidently dependent on the quantized angles adopted by the bond orbits. The transmission through a long chain of a property imposed by a substituent would also seem to be

possible only when the moment of the trunk does not interfere. With oxygen and nitrogen where energy is locked up between trunk and orbits, the configuration will not have the freedom possible in the case of saturated carbon. Since the hypothesis expressed in equation (10) restricts the possible angles which can be assumed by the orbits to the values  $\cos \theta_1 = 1, 2/3$ , and  $1/3$ , when the trunks have no moment they must lie in the plane of the common orbits. Thus the spatial quantizing of the orbits necessarily implies in the case of carbon the definite orientation of the trunks.

As has been stated, the most symmetrical arrangement of orbits in carbon is that illustrated in fig. 2 (a), where three bonds at  $\cos \theta_1 = 1/3$  are in equilibrium with one at  $\cos \theta_1 = -1$ . Each of the angles between bonds then becomes the well-known "tetrahedral" angle  $109^\circ 28'$ .

Fig. 2.



If, on the other hand, the moment on one side of the equatorial plane is altered so that it becomes equal to  $3 \cdot 2 + 1/2 = 2$ , the remaining three bonds on the other side must adopt the  $\cos \theta_1 = 2/3$  position as shown in fig. 2 (b). The angle  $\theta_1$  now becomes  $131^\circ 47'$ . It is therefore a definite consequence of the theory that the "tetrahedral" angle is not the only angle which must be taken into account in explaining the stereoisomerism of carbon compounds. If we consider a chain of carbon atoms united by bonds forming these two angles with the direction of the field, which will be at right angles to the length of the chain (fig. 3, a and b), the distance between each successive carbon atom will be proportional to  $\sin(\cos^{-1} 1/3)$  and  $\sin(\cos^{-1} 2/3)$  respectively. The ratio of these numbers will represent the relative rate of increase in length of a carbon chain connected by bonds at these angles.

From X-ray measurements, quoted by Bragg (Trans. Farad. Soc. Discussion, 1923, p. 478), Muller and Shearer have shown that the molecules of fatty esters orientate themselves in thin films in such a way that their length is at right angles to the surface, "like the stalks of growing corn." Increase in the length of the acid end of the molecule produces an increase in thickness at a different rate from increase in the alcohol radicle. They find that these increases are in the ratio

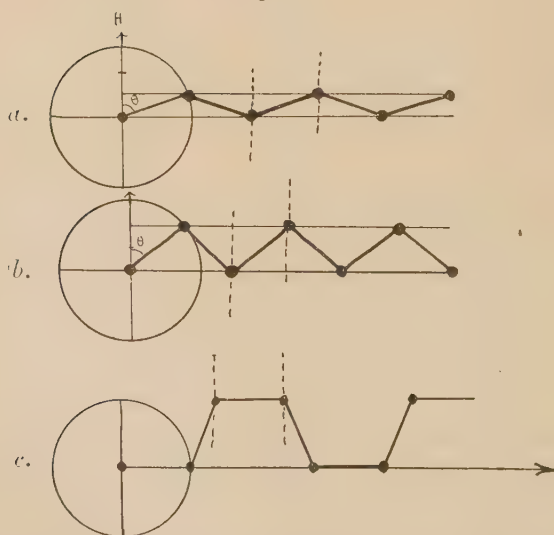
$$\frac{2 \text{ acid radicle carbons}}{1 \text{ alcohol ,, carbon}} = \frac{1.94}{1.22} = 1.59.$$

If we identify the bond angle characteristic of the acid end of the molecule with the  $\cos \theta = 2/3$  position, we should have theoretically,

$$\frac{2 \text{ bonds at } \cos^{-1} 2/3}{1 \text{ ,, ,, ,, } 1/3} = \frac{2 \times \sin (\cos^{-1} 2/3)}{\sin (\cos^{-1} 1/3)},$$

$$\frac{2 \times 0.7455}{0.9428} = 1.58.$$

Fig. 3.



This is a remarkable agreement which affords definite experimental support to the consequence of this theory which demands three possible bond angles for carbon. The



explanation suggested by Bragg (*loc. cit.*) is inherently improbable as it denies the possibility of free rotation about a single bond. This will be clear from a comparison of *a*, *b*, and *c* in fig. 3. The bonds in *a* and *b* are free to rotate about the dotted lines without distortion of the bond angle, or alteration in the distance between carbon atoms. Free rotation in *c* must produce the same length of chain as in *a*.

The insight into structural relations of carbon compounds which the theory affords will be developed in a paper to follow shortly. The treatment of the polar link, which, as has been stated, stands in the same relation to the non-polar link treated above as does the Stark effect to the Zeeman effect, has been worked out satisfactorily, and will follow as Part II. of this series.

*Note.*—Since the original of this paper, and those to follow, was written, the author has considered the application of the extremely interesting theory of the quantum relation published by de Broglie (*Phil. Mag.* xlvii. p. 446, 1924). It is worth noting here that the fundamental principle of the synchronization of bond orbits follows directly from de Broglie's generalization that for stable orbital motion "the phase wave is tuned with the length of the path."

Simla,  
August 1924.

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XXXVIII. *Short Electric Waves obtained by the use of Secondary Emission.* By E. W. B. GILL, M.A., B.Sc., Fellow of Merton College, Oxford, and J. H. MORRELL, M.A., Magdalen College, Oxford\*.

IN a previous communication (*Phil. Mag.* July 1922) the authors gave an account of some experiments on the production of continuous oscillations of short wavelengths of the order of a metre by gas-free valves, and put forward a theory to account for their maintenance. The theory was only worked out for the case where the electron currents through the valves were small and the space charges between the electrodes negligible, if the currents are large the theory would have to be modified.

In all cases, however, the main conclusion was correct, that if the time *T* that the electrons in the valve take to pass from one electrode to another is comparable to the time *t* of

\* Communicated by Prof. Townsend.

*Phil. Mag.* S. 6. Vol. 49. No. 290. Feb. 1925. 2 B

oscillation of the attached circuits, then a control electrode as usually employed is not necessary, since for certain values of the ratio  $T/t$  the motion of the electrons will vary in such a way that they maintain the oscillations.

These considerations lead to the fact that a particular applied voltage maintains most strongly an oscillation of a particular wave-length: a species of "tuning" which is non-existent for longer wave-lengths maintained by the more usual methods.

In the first experiments the oscillations were produced in a Lecher wire system attached to the grid and plate of a 3-electrode valve, the filament and plate being at about the same potential and the grid several hundred volts positive to them; this method of short wave production was discovered by Barkhausen and Kurz (*Physikalischer Zeitschrift*, Jan. 1920). In this arrangement the electrons moving from the filament are accelerated in the space between the filament and the grid, and are retarded between the grid and the plate.

In the experiments to be described the grid has still the highest positive potential, but the plate, instead of being at about the same potential as the filament, is also at a fairly high positive potential. In this case all the electrons which pass through the grid reach the plate whether oscillations are occurring or not, and the secondary emission from the plate becomes of importance.

It may be convenient to state briefly the main effects of secondary emission in a 3-electrode valve.

If in such a valve the grid is maintained at a fixed high positive potential  $V_g$  above the filament\*, and the plate current is found for various plate potentials  $V_p$  above the filament, the relations between the plate current and the plate potential are given by curves as in fig. 1, as found originally by Hull†. In these curves the negative current through the valve to the plate is plotted upwards.

The electrons move from the hot filament to the grid under an accelerating potential  $V_g$ , those which pass through move on to the plate under a retarding potential  $V_g - V_p$  and strike the plate with the velocity acquired by falling through a potential difference  $V_p$ . As a result of this impact secondary electrons are emitted from the plate with a negligible

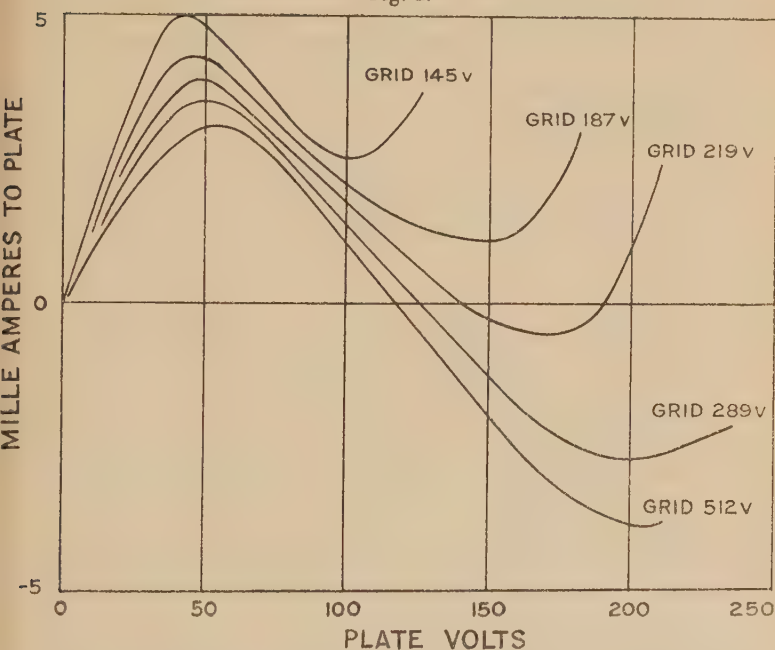
\* In this paper the filament is taken as at zero potential, the voltage drop down it is neglected, and no account is taken of velocities of emission or contact differences of potential.

† Hull, Proc. Inst. Radio Engineers, Feb. 1918.

velocity and move to the grid under the accelerating potential  $V_g - V_p$ . The reduction of the current with increase of plate potential, as shown by the curves, is due to this emission. As the velocity of impact (which depends only on  $V_p$ ) is increased the number of secondary electrons increases.

It is not necessary to discuss the upward bend of the current when  $V_p$  is further increased, as the oscillations to be described could not be maintained for values of  $V_p$  in this region\*.

Fig. 1.



The downward portions of the curves are nearly straight lines and it is very fairly accurate to assume, as will be done, that the number of secondary electrons set free by  $n$  primary electrons, if the plate potential is  $V$ , is proportional to  $nV$ .

It should be noted that for the filament emissions and particular values of  $V_g$  and  $V_p$  used, none of the electrons emitted from the filament return to it and none of the secondaries return to the plate. The voltages are sufficient

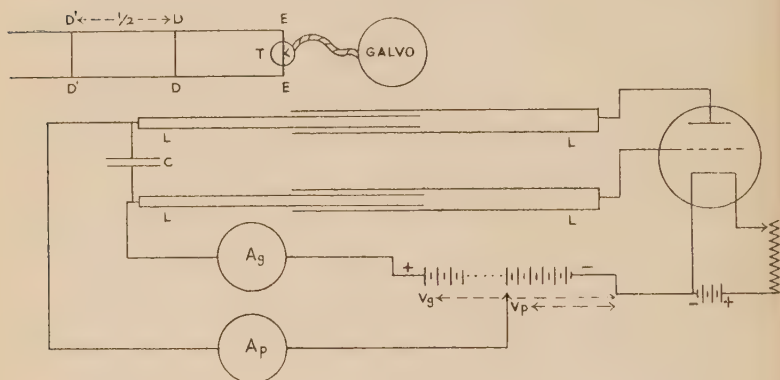
\* A detailed explanation of the curves is given in Phil. Mag. May 1923, p. 864.

to collect the saturation currents, both from the filament and the plate, and the space charges, although they modify the fields due to the fixed potentials  $V_g$  and  $V_p$ , cannot be the ultimate cause of the maintenance of oscillation. The case is therefore entirely different from the usual methods of producing oscillations by valves in which the control of the space charge by the grid potential is the essential feature.

Two types of 3-electrode valves were used in the experiments:—A Marconi MT 5 type (described in detail, *Phil. Mag.* July 1922, p. 165), and a Marconi LS type which has a tungsten filament, the grid is a spiral of molybdenum wire of diameter 5 mm., and the plate is a cylinder of nickel of diameter 10 mm. The LS is smaller than the MT 5, which has a grid 10 mm. in diameter and plate 25 mm. diameter.

The circuits used are shown in fig. 2.

Fig. 2.



The oscillatory system consisted of two Lecher wires  $LL$  attached respectively to the grid and the plate of the valve, the other ends of the wires being bridged by the condenser  $C$  of about 1 mmf. capacity. The length of the Lecher wires was adjustable, each being made of a telescopic tube sliding over a rod.

The oscillatory system thus comprised distributed inductance and capacity of the wires and concentrated capacities at both ends; the plate and grid of the valve forming a small cylindrical condenser.

The condenser  $C$  was by far the largest capacity in the circuit, so that its terminals may be regarded as potential nodes for any oscillation in the system and suitable points for attaching the leads to the high potential battery. This

high potential battery was used to maintain the grid at a high positive potential  $V_g$  above the filament (negative end) and the plate at a positive potential  $V_p$  less than  $V_g$ , milliammeters  $A_g A_p$  indicated the currents flowing to the grid and plate respectively.

The wave-lengths and relative magnitudes of any oscillatory currents set up were determined by means of a secondary circuit loosely coupled to the valve circuit. This secondary circuit also consisted of Lecher wires L, L, about 10 cm. apart, bridged at one end EE by wires to the heater coil of a Paul thermo-couple T, which had a sensitive galvanometer attached to the thermo-couple. The wires were also bridged by a sliding bar DD.

The method of carrying out an experiment is the following. The filament is heated to a suitable brightness, and a simple preliminary test made to see if oscillations are occurring in the Lecher wire system attached to the valve; this is easily done by touching various points of the wires with the hand. If oscillations are taking place this process damps them and the readings of the milliammeters AA change.

If this test indicates that there are no oscillations, the telescopic rods are pushed in or out till a sudden change in the readings of the milliammeters indicates that oscillations have commenced. The bar DD is now moved along the secondary circuit, and when the circuit DEED is in tune with the primary the galvanometer attached to T shows its maximum deflexion; it will reach a second maximum when DD is moved a further distance  $\lambda/2$ ,  $\lambda$  being the wave-length.

The use of the secondary circuit gives the wave-length of the primary oscillation, and the maximum galvanometer deflexion is proportional to the square of the primary current provided the relative positions of the two circuits are always the same.

It would have been simpler to measure the magnitude of the primary oscillatory current direct by inserting the thermo-junction in that circuit, but it was found that the resistance of the junction made the maintenance of the oscillation, which was always very feeble, extremely difficult.

By experiments of the type outlined above it was found that for a fixed value of  $V_p$  and  $V_g$  oscillations could be maintained over a certain range of wave-lengths (just as the authors found for the Barkhausen short waves)

Thus with the MT 5 valve the grid charged to 312 volts positive to the filament and the plate to 127 volts; it was



found that oscillations could be sustained from  $\lambda=176$  cm. to  $\lambda=194$  cm. For 176 cm. the oscillation was just detectable: as  $\lambda$  was increased the amplitude of the oscillation increased till at 188 cm. it reached its maximum. From 188 cm. to 194 cm. the amplitude decreased.

For a larger electron emission from the filament the range of wave-lengths over which oscillations could be sustained was increased, but the maximum oscillation still occurred at about  $\lambda=188$ .

Confining attention now to the wave-length of the oscillation with the maximum current amplitude, the next point to be investigated was how  $\lambda$  depends on the potentials of the electrodes.

The result of many experiments with the LS valve done in the method described indicated :—

(A) That if  $V_g - V_p$  was kept constant the wave-lengths of strongest oscillation were within errors of experiment independent of the absolute values of  $V_g$  and  $V_p$ .

Thus with the LS valve the values of  $\lambda$  found under such a condition were :—

$V_g$ .	$V_p$ .	$V_g - V_p$ .	$\lambda$ in cm.
122 volts	38	84	101.6
164	78	86	99.4
208	122	86	98.6

(B) That if  $V_p$  was kept constant and  $V_g - V_p$  varied, then  $\lambda^2(V_g - V_p)$  was constant within errors of experiment.

Thus with LS valve for  $V_p$  constant and various values of  $V_g - V_p$ , the values of  $\lambda$  and of  $\lambda^2(V_g - V_p)$  were :—

$V_p$ .	$V_g$ .	$V_g - V_p$ .	$\lambda$ .	$\lambda^2(V_g - V_p)$ .
160	244	84	94.6 cm.	$751 \times 10^3$
160	272	112	82.1	754 "
160	291	131	75.6	748 "
160	299	139	74	761 "

(C) As mentioned previously, oscillations could not be maintained if  $V_p$  was so nearly equal to  $V_g$  that the corresponding point in fig. 1 was to the right of the downward portion of the curve.

The combination of A and B indicates that whatever the values of  $V_g$  and  $V_p$  the wave-length  $\lambda$  depends only on  $V_g - V_p$  in accordance with the formula  $\lambda^2(V_g - V_p) = \text{const.}$

This suggests that the electrons responsible for the maintenance of the oscillations are the secondary electrons which

go from the plate to the grid as their time of passage depends on  $V_g - V_p$  only. For the primary electrons pass from the filament to the grid in a time which depends on  $V_g$ , they pass through the grid with a velocity depending on  $V_g$ , and their time from the grid to the plate depends therefore on  $V_g$  as well as on  $V_g - V_p$ .

The following calculations show that oscillations of the type observed can be maintained by the secondary electrons.

The energy conditions for the maintenance of an oscillation are simple. If an oscillation is started in the circuits connected to the valve, alternating potential differences are set up between the electrodes. The electrons moving across the valve are acted on by these alternating potentials as well as by the fixed potentials applied to the electrodes. If the alternating potentials do work on the electrons, this work is done at the expense of the energy of the oscillations and in consequence the oscillations are damped out; if, on the other hand, the work done by the alternating potentials on the electrons is negative, the oscillation will be sustained. The electrons in this latter case give energy to the oscillating circuit which can be sufficient to compensate it for resistance and radiation losses.

(When the oscillations are being sustained the electrons hit the electrodes with less velocity than when there are no oscillations; the heating of the plate is thus less in the former than the latter case, and the difference represents the work available for the maintenance of the oscillations.)

It may be assumed that the alternating potential between plate and grid is  $V_0 \sin pt$ , with periodic time  $\frac{2\pi}{p}$ .

The filament is joined to potential nodes on the Lecher wire system, and its potential being taken at zero, the total plate potential at time  $t$  is  $V_p + \frac{1}{2}V_0 \sin pt$ , and the total grid potential is  $V_g - \frac{1}{2}V_0 \sin pt$ .

The following simplifying assumptions will be made:—

1.  $V_0$  is so very small compared with  $V_p$  and  $V_g$  that the time the electrons take to move between the electrodes is determined only by  $V_p$  and  $V_g$ , not by  $V_0$ .
2. The plate and grid will be regarded not as concentric cylinders but as parallel planes at distance  $d$  apart.
3. The secondary electrons will be supposed to leave the plate with zero velocity and to move direct from the plate to the grid and none to pass through the grid.
4. The effect of space charges will be neglected.

The electrons moving across the valve can be divided into three classes. The first, those which go direct from the hot filament to the grid; the second, those which go from the filament to the plate; the third, the secondary electrons which return from the plate to the grid.

It can be shown that the work done per cycle by the alternating potentials is zero for both the first and the second class, and it is only necessary therefore to consider the last class.

Let  $T$  be the time the secondary electrons take to pass from the plate to the grid, which in accordance with assumption 1 is the same for all and is equal to

$$d\sqrt{\frac{2m}{e(V_g - V_p)}}.$$

The electron which leaves the plate at time  $t_0$  has at time  $t$  a velocity given by

$$\frac{dx}{dt} = f(t - t_0),$$

where

$$f = \frac{e}{m} \frac{V_g - V_p}{d},$$

the axis of  $x$  being normal to the plate.

The work done by the alternating potential  $V_0 \sin pt$  as the electron moves from the plate to the grid is

$$- \frac{eV_0}{d} \int_{t_0}^{t_0+T} \sin pt \cdot dx,$$

which on integration becomes

$$- \frac{feV_0}{d} \left\{ \frac{\sin p(t_0 + T)}{p^2} - \sin pt_0 - \frac{T \cos p(t_0 + T)}{p} \right\}. \quad (1)$$

If the electrons left the plate in a uniform stream the average value of the expression (1),  $t_0$  being regarded as the variable and having values from 0 to  $2\pi/p$ , would be zero.

The secondary stream is not however uniform, for as  $t$  varies the primary electrons hit the plate at different velocities corresponding to falling through a potential drop of  $V_p + \frac{1}{2}V_0 \sin pt$ . Remembering that the number of secondary electrons emitted for each incident primary is approximately proportional to the potential through which the incident electron has fallen, the number of secondaries given off between time  $t_0$  and  $t_0 + dt_0$  is proportional to

$$(V_p + \frac{1}{2}V_0 \sin pt_0) dt_0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The work done per cycle by the alternating potential on the secondary electrons is therefore proportional to the integral between  $t_0=0$  and  $t_0=2\pi/p$  of the product of expressions 1 and 2. Omitting certain constants, the work per cycle is thus found to be proportional to

$$-\frac{1}{p^3} \{ \cos pT - pT \sin pT - 1 \},$$

or the work per second is proportional to

$$-\frac{1}{p^2} \{ \cos pT + pT \sin pT - 1 \}.$$

Hence, if  $T_0$  is the time of one oscillation,  $T_0=2\pi/p$  and the work is proportional to

$$-T_0^2 \left\{ \cos 2\pi \frac{T}{T_0} + 2\pi \frac{T}{T_0} \sin 2\pi \frac{T}{T_0} - 1 \right\}.$$

The energy communicated to the oscillating system per second by the electrons is therefore proportional to

$$T_0^2 \left\{ \cos 2\pi \frac{T}{T_0} + 2\pi \frac{T}{T_0} \sin 2\pi \frac{T}{T_0} - 1 \right\},$$

and oscillations will be maintained if this expression is positive and the energy is equal to that lost by resistance and radiation.

If  $V_g$  and  $V_p$  are kept constant,  $T$ , which is proportional to  $\frac{1}{\sqrt{V_g - V_p}}$ , is constant, and the wave-lengths which can be maintained are those for which  $T_0$  makes the above expression positive.

Keeping  $T$  constant, the variations of the value of this work function as  $T_0$  is varied are given in the following table :—

Value of $\frac{T_0}{T}$ .	Value of function.	Value of $\frac{T_0}{T}$ for maximum energy.	Value of $\frac{T_0}{T}$ for zero energy.
$\infty$ to 2·7	{ Positive and decreasing.	$\frac{T_0}{T} = \infty$	$\frac{T_0}{T} = 2·7$
2·7 to 1	Negative.	.....	$\frac{T_0}{T} = 1·0$
1·0 to ·66	Positive.	$\frac{T_0}{T} = 0·8$	$\frac{T_0}{T} = 0·66$

and so on alternately positive and negative.

If for convenience we call  $\lambda$  the wave-length of the oscillation whose periodic time is  $T$ , then the energy conditions are suitable for the maintenance of all waves longer than  $2.7\lambda$ ; not suitable for waves between  $2.7\lambda$  and  $\lambda$ , suitable for waves from  $\lambda$  to  $.66\lambda$  and so on, while with regard to the range from  $\lambda$  to  $.66\lambda$  the wave-length which is most strongly regenerated is  $.8\lambda$ .

It is this range which the preceding experiments have evidently covered; for we found that a small range of wave-lengths was maintained. Further, as the strongest regeneration occurs for the particular value  $.8$  of  $\frac{T_0}{T}$ , we should expect that if  $T$  is altered the wave-length of maximum amplitude should alter in the same ratio, but  $T$  is proportional to  $\frac{1}{\sqrt{V_g - V_p}}$ , and it is therefore to be expected that the wave-length of maximum amplitude should also be proportional to  $\frac{1}{\sqrt{V_g - V_p}}$ , which was found to be true.

The broadening of the range if the filament is heated more brightly is accounted for by the fact that more electrons leave the filament per second and more energy is therefore available to compensate for the oscillation losses. The theory indicates that there should be other ranges of still shorter wave-length maintained which we did not get experimentally; but this was to be expected, as the energy losses increase enormously as the wave-length gets very small.

With regard to the longer wave-lengths it was from the outset probable that these would be maintained as the circuit is a modified form of Hull's well-known "negative resistance" method of producing continuous oscillations.

A final test was made with the MT 5 valve with  $V_g - V_p = 180$  volts, and it was found that wave-lengths above .33 metres, and below this the range from 1.94 metres to 1.76 metres, could be maintained.

The general experimental results that all wave-lengths above a certain value, and a range of shorter wave-lengths, can be maintained are in good agreement with the theory. The agreement when numerical values are calculated is not so good. In the first place, the gap between the shortest long wave maintained and the best maintained short wave is larger than would be expected from the theory, and in the second place, if the time  $T$  that an electron takes to pass



from the plate to the grid is calculated from the valve dimensions the ratio  $\frac{T_0}{T}$  for the best maintained short wave is not .8 as the theory gives, but about 2 for the LS valve and 3 for the MT 5.

With regard to the first point, the simple theory gave an expression for the work put into the oscillatory circuit per second for different wave-lengths for a specified amplitude  $V_0$  of alternating potential between the grid and the plate. This work must be equal to the resistance and radiation losses per second for the oscillatory current corresponding to this value  $V_0$ . For a small variation in wave-length this current is proportional to  $V_0$ , but this is not the case for large variations of the wave-length, as the distributed capacity of the wires must be taken into account. It does not necessarily follow therefore that if the work function has a particular value for a short wave-length which is maintained, that the long wave for which the work function has the same value will also be maintained.

With regard to the second point, it is probable that the assumption that none of the secondary electrons pass through the grid chiefly accounts for the discrepancy, and that many of them pass backwards and forwards once or twice through the grid before being collected on it,—in fact the theory on which the calculations are based can only be expected to account for the main features of the experiments.

We are very much indebted to Professor Townsend for help and advice in these experiments.

### XXXIX. *On the Discriminations between Past and Future.*

*By P. DU VAL\*.*

**T**HIS paper is intended to supplement and develop some remarks on the subject in my "Geometrical Notes on de Sitter's World" (Phil. Mag. May 1924).

In the first case it is important to notice that the consciousness of an observer is related to his past and his future in ways far more strikingly different than the mere geometry of the question would lead us to suppose.

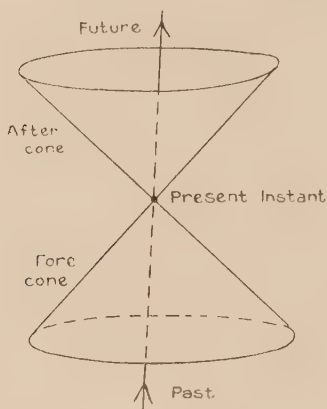
Thus, his world-line passes at the "present instant" through the vertex of the light-cone, being within the cone

\* Communicated by the Author.

on both sides of the vertex, as in fig. 1. Both cone and world-line are divided at the vertex into two portions extending to infinity, one segment of the line being within each sheet of the cone and outside the other.

Now, of course, most observers can by the exercise of their intellectual faculties form some conception of what events lie in various parts of the world, both on and off their own world-lines; but each observer has a peculiarly distinct consciousness, quite intuitive and arrived at without logical procedure, of certain events which can only be regarded as forming a part of the "here and now" of his perceptual experience.

Fig. 1.



These are the events of one sheet of his instantaneous light-cone, which we call the fore-cone, and of one segment of his world-line, which we call the past segment, the past segment of the world-line being that one which lies inside the fore-sheet of the cone (fig. 1). The observer's perceptions of these two loci of events, superficially very dissimilar—one being what we call memory and the other vision—have yet this resemblance, that both are of geometrical loci, abruptly broken off at the "present instant," where the consciousness in each case rises to a maximum of intensity, while it shades off into dimness and ultimate oblivion in the direction of infinity.

This odd fact, that we are conscious of half the events in our light-cones and half those in our world-lines (that is, speaking roughly; of course no one can remember all the past, or see an infinite distance; but we are accustomed to consider hypothetical observers of infinite longevity), which

is by no means to be expected from the current geometrical view of the world, is of the utmost empirical importance, having in fact conditioned our whole attitude towards that dependence of events on one another which we call causation. Indeed, it is just our certain intuitive knowledge of events on the past side of us, and our total ignorance (except by inference) of those on the future side, which make us regard the former as fixed, and as determining our present experience, while we regard the latter as depending on the at least partly arbitrary course of our present conduct. To put it more clearly, when we consider the relation between past and present events, we habitually regard the past as argument and the present as function, while in the contrary case we regard the present as argument and the future as function, oblivious of the fact that the relation between function and argument is ordinarily a reversible one, either equally determining the other.

We can bring the fictitious nature of our view of causation home to ourselves by considering a slightly different arrangement. Suppose, for instance, the fore-sheet of the cone to be that which contains the future segment of the world-line; in such a case our present attitude, if adhered to, would force us to conclude that some influence, issuing from our eyes with the speed of light, is a determining cause of the events which we see, since by any ordinary standard of time-measurement we should see them before they happened.

It is thus important, for the understanding of the history of any observer, not only to draw his world-line, and mark on it a scale of proper-time, but to indicate the sense in which this proper-time is to be reckoned. It is also a matter of the first importance whether this sense is determined at random for each observer separately, or whether it depends in some way on the constitution of the world as a whole, and also whether there is any way in which we can define same and opposite senses in two different world-lines. The answers to these questions are of course different in different worlds, but a few general remarks are possible.

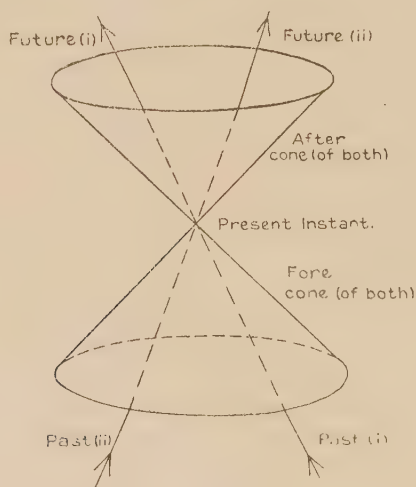
For instance, if two world-lines intersect, sameness or opposition of sense in them is perfectly definable with reference to this particular intersection, since they have here the same light-cone, and hence determinately the same or opposite discriminations between its two sheets.

Thus in fig. 2 the observers (i) and (ii) are oriented in the same sense, whereas if the past and future of one of them were interchanged, the fore-cone of each would be the

after-cone of the other, and their senses would thus be opposed.

In this connexion, it should be borne in mind that it is quite easy to devise a world in which two world-lines may intersect twice, and that in such a way that senses in them which are the same with reference to one intersection are opposed with reference to the other.

Fig. 2.

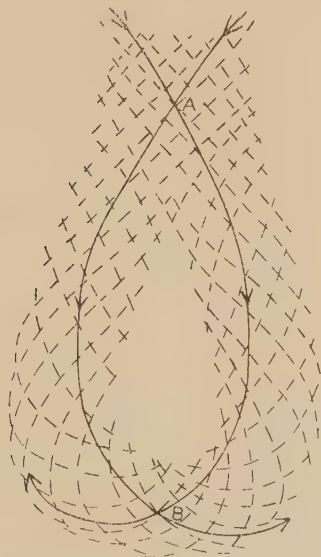


For instance, in the world of loop-like connectivity shown in fig. 3 (where the broken lines indicate the general direction of the light-tracks) we can draw two world-lines intersecting at A and B, and give them senses which are the same relatively to the light-cone at A, but opposite relatively to that at B.

Another case in which sameness or opposition of sense is definable is that of two lines which throughout a considerable length have every point of each at a comparatively small distance from some part of the other. Lines thus related we may call *paralleloid*. Thus, if A in one line is quite close to A' in the other, and B (distant from A) close to B' (distant from B), and so for every intervening point, the sense AB may clearly be looked on as the same as A'B' and opposite to B'A'. In this case again, the sameness or opposition of sense can only be regarded as referring to the region in which the world-lines are *paralleloid*; for in a world such as

that illustrated in fig. 3, we could draw two lines parallel in two regions, and such that senses in them which were the same with reference to one region were opposed with reference to the other. Indeed, a consideration of the figure shows that we could make a world-line to intersect (or to be parallel to) itself, such that in whichever sense it is measured, the two intersecting (or parallel) parts are oppositely directed.

Fig. 3.



This case of parallelism is important, as all the particles of the Earth, indeed one might say the solar system, are in parallel world-lines; and it is clear that at least the entire human race, apparently the whole sentient population of the globe, have their consciousness in the same sense. In deciding the merits of any particular world which may be proposed as representing that in which we live, this fact must be borne in mind, and a hypothetical world which offers no explanation of it must be felt to have a very serious disadvantage.

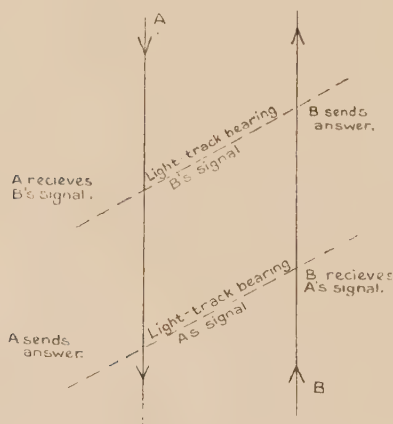
It is an amusing exercise to imagine the case of two observers with oppositely directed consciousness in parallel



world-lines. No kind of communication is possible between them, since if one sends a signal and the other receives it, it at once (from the point of view of the former) passes into the latter's not-yet-happened-future, and he, ignorant of its nature, even of its existence, cannot possibly answer it.

Fig. 4 may serve to illustrate this. Each of the two observers A, B, receives (the emission of it being on his fore-cone) a visual signal from the other, and at a later instant (from his own point of view) sends off his answer to it. This is a striking instance of the breakdown of our notions of causation, since here each observer regards his own signal as the answer to, *i.e.* as caused by, the other;

Fig. 4.



while neither is conscious of having taken the initiative in the attempt at communication. On a superficial view it would thus appear that the whole thing happened of its own accord, without any external cause, even in the volition of the participants; though of course it will in fact be co-dependent with other events, both before and after it.

It is worth considering also the appearance of the world to a human observer whose sense is reversed throughout a finite length of his world-line. (Our knowledge of the laws which govern time-consciousness is hardly sufficient to enable us to rule this possibility out categorically, though I admit it is rather entertaining than probable.) The instant of the first reversal of sense would appear to him to be followed without break by that immediately before the restoration of

the original sense, events then proceeding like a cinematograph show in which the film is sent through the lantern wrong end first till the instant of the first change is reached, that being at once followed by the return to normal conditions, and the succeeding events in their proper order. During his period of abnormality a person writing (for instance) would seem to him to pass his pen backwards over the written paper, sucking up every scrap of ink into the nib, so that all trace of what originally appeared written would be removed; if he himself was stunned by a fall, he would (in his own opinion) wake suddenly to the sensation of being flung up from the ground and landed neatly in the spot from which in point of fact he fell; an object knocked down and smashed would be seen first as fragments strewn on the ground, which would with one accord seem to leap together to form the broken object, and rise into its proper position. Such instances could be continued indefinitely.

As for the question how far the sense of an observer's time-consciousness may depend on the general structure of the world, it may be simplified by observing that a world-line in which  $s$  is the proper-time will contain in general two "points at infinity,"  $s = \pm \infty$ . All the points at infinity in all the possible world-lines in the world will ordinarily form a three-dimensional locus, though of course in special cases it may degenerate into a surface, a curve, or a point or points. If this locus is such as to supply a determinate distinction between  $s = +\infty$  and  $s = -\infty$  in every line, each observer's sense is determined by the general structure of the world; not otherwise. There is one other possible case—the world-lines may be re-entrant, without any points at infinity. In such a case it will ordinarily be found possible to construct a three-dimensional locus, cutting each line once, and so providing each with a beginning and end.

Excellent examples of the two non-reentrant cases are furnished by the two cases of de Sitter's world. In the spherical world, as I pointed out in my Note already referred to, the locus of points at infinity consists of two entirely distinct branches, and every world-line meets each branch of the locus once. It is thus clear that we can assign to all the points on one branch the coordinate  $s = +\infty$  for all the world-lines on which they lie, and to all on the other branch  $s = -\infty$ , so obtaining a general distinction between the past and future of every observer. Figs. 5 and 6 make it further obvious that these discriminations are the same for intersecting or paralleloid world-lines.

Fig. 5 shows two intersecting world-lines in which the proper-times are  $s_1$  and  $s_2$ , with the section of the light-cone at their point of intersection. Fig. 6 shows two parallel world-lines.

Thus in this world the only arbitrary feature is the initial choice which branch of the locus we will call the "Beginning" and which the "End of Eternity."

Fig. 5.

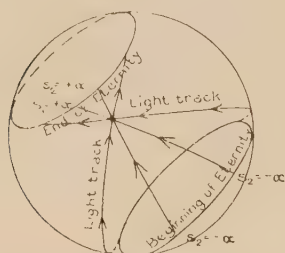
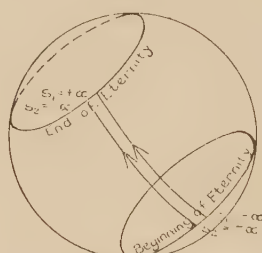
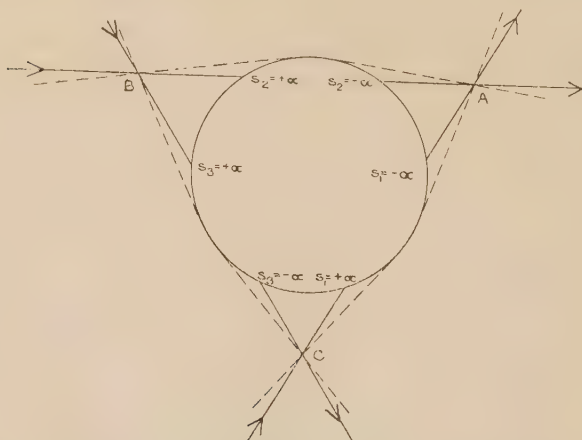


Fig. 6.



In de Sitter's Elliptic world, however, the case is quite different. The locus consists of one branch only and any two points on it whatever may be two points at infinity on a world-line. Clearly no general discrimination between past

Fig. 7.



and future is here possible; and we can easily construct three lines intersecting in pairs, such that not all three pairs can possibly be measured in the same sense. Thus in fig. 7—which is in the Cayley-Klein projection—whereas the proper-times  $s_1$ ,  $s_2$  are measured in the same sense with reference to the intersection A, and  $s_2$  and  $s_3$  are all in the same sense

with reference to B,  $s_3$  and  $s_1$  are in opposite senses with reference to C.

Before, however, we utterly reject the elliptic world (which, to me at least, seems to have in other respects decided advantages over the spherical) as a description of actual phenomena, we shall do well to remember that neither claims to be more than a first approximation, and that the sameness of sense of the inhabitants of the earth may perhaps be explained in terms of the departures from de Sitter's metric, which constitute the matter of the world. For instance, the world-lines of all the objects which compose the Earth, including the bodies of sentient observers on its surface, form a sort of rope of myriads of strands, indefinite (probably infinite) in length and roughly constant in thickness, twisted (since the Earth as a whole rotates) and matted—on the surface at any rate—to an indescribable complexity. Now the diameter of the tubular region containing this rope is very small indeed compared with even so much of its length as is known to us (using 1 sec. =  $3 \times 10^{10}$  cm. as basis of comparison), and is also very small compared with the radius of curvature of the world; so that all the world-lines are parallel, and (at any rate throughout the known history of the Earth) same-ness of sense between them is definable and transitive, just as in the spherical world. This arrangement is clearly conditioned by the structure of the world, since the uniformly small thickness of the rope, and its non-confusion with other world-lines, depend on the law of gravitation, itself an expression of an aspect of the metrical constitution of the world.

An equally elementary instance of a world with re-entrant world-lines is offered by one remarkably similar to de Sitter's. It is interesting as being the only (3+1)-dimensional world besides those of de Sitter and Minkowski which is discussible in terms of projective geometry by the introduction of a quadric "absolute." Like de Sitter's world, the absolute divides it into two fields, one only of which is (3+1)-dimensional. Taking Wierstrassian coordinates  $x_1, x_2, y_1, y_2, y_3$ , we have for the absolute

$$\Sigma(x^2) = \Sigma(y^2),$$

and the (3+1)-dimensional field (which we may call actual) is that in which

$$\Sigma(x^2) > \Sigma(y^2).$$

The most convenient restriction is thus

$$\Sigma(x^2) - \Sigma(y^2) = 1,$$

which is satisfied by the values (in terms of four parameters)

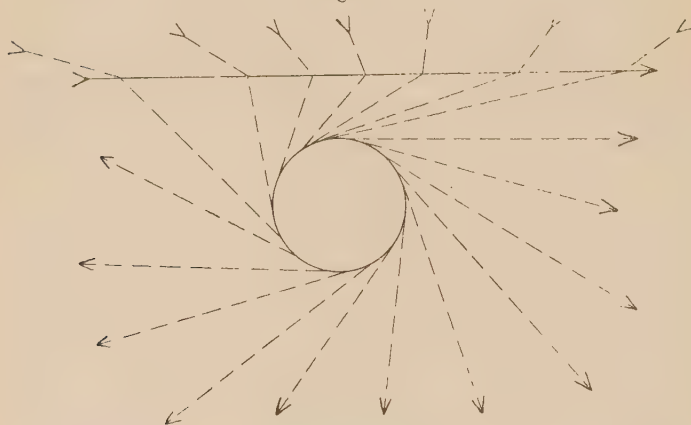
$$\begin{aligned}x_1 &= \cosh \chi \cos t, \\x_2 &= \cosh \chi \sin t, \\y_1 &= \sinh \chi \cos \theta, \\y_2 &= \sinh \chi \cos \theta \cos \phi, \\y_3 &= \sinh \chi \cos \theta \sin \phi.\end{aligned}$$

The element of length is given (in "natural" units) by

$$\begin{aligned}ds^2 &= \Sigma(dx^2) - \Sigma(dy^2) \\&= \cosh^2 \chi dt^2 - [d\chi^2 + \sinh^2 \chi (d\theta^2 + \sin^2 \theta d\phi^2)]\end{aligned}$$

The negative portion of this is the ordinary 3-dimensional hyperbolic metric; thus the instantaneous space is hyperbolic; time, however, as shown by the values of  $x_1, x_2$ , is

Fig. 8.



re-entrant, every world-line having the finite length  $\pi$  or  $2\pi$  according as we choose the elliptic or spherical case. Thus the absolute encloses the world as a re-entrant sheath rather like the "anchor-ring," the  $(3+1)$ -dimensional world corresponding to the region within the ring, and any world-line to a closed curve threaded right round the ring.

In this illustration we see that it is permissible to speak of a sense this way or that round the ring as a whole, and that two world-lines have determinately the same or opposite senses. Figs. 8 and 9 show an observer's world-line, the fore-cone at all points, and the absolute, in a two-dimensional section, such as  $\theta = \phi = 0$ , so projected that the absolute

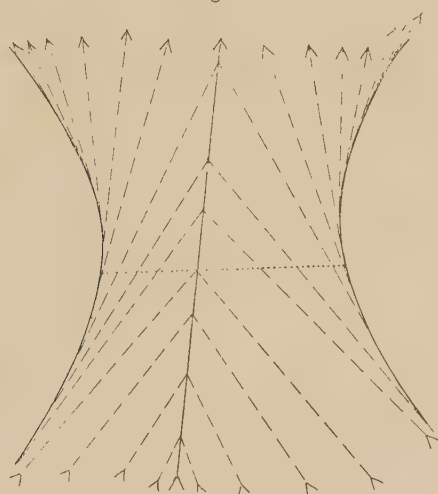


becomes an ellipse in the one case and an hyperbola in the other.

These figures make clear the continuity of sense of the light-tracks (*cf.* fig. 5 in my Note on de Sitter's world).

Now let us give the world a fictitious beginning, and end by slicing it across along an instantaneous space ( $t = \text{const.}$ ), as shown by the dotted line in fig. 9. This flat space has two distinct faces (corresponding to the two faces of a plane in the three-dimensional geometry); one face contains the "beginning" of the world-line, and the "beginnings" also of all the light-tracks which meet it, the other contains all the corresponding "ends." Thus we can with perfect consistency make the "beginnings" of all world-lines and all

Fig. 9.



light-tracks lie in the one face, and their "ends" all in the other; which leaves sameness of sense determinate and transitive.

As (so far as I know) this world has not before been publicly discussed, it may be worth pointing out that most of its properties can be derived from de Sitter's world by a simple imaginary substitution. Real values of the coordinates  $(t, \chi, \theta, \phi)$  can be assigned to every point; as in de Sitter's world  $t = \text{const.}$  are flat spaces, but they intersect in a plane in the ideal field (beyond the absolute) so that there is no horizon;  $\chi = \text{const.}$  are quadrics tending towards the absolute as  $\chi$  approaches  $\infty$ . Motion under the cosmic force is periodic

and isochronous, in accordance with the re-entrant character of the time-axis, but (as Prof. Eddington has pointed out to me) the isochronous property is destroyed by the introduction of gravitating bodies, so that it is unlikely that this world will prove of value as a hypothetical approximation to the actual one.

These three worlds have been discussed at perhaps unnecessary length, as instances of the way in which the problem may be approached; what has already been said is, I hope, enough to draw attention to this important question of the sense of time, which seems to me to demand very close investigation, both by the geometer and by the philosopher.

XL. *A Note on Dr. Turner's Paper "Quantum Defect and Atomic Number."*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

I SHALL be glad if you will allow me to make some comments on a paper by Dr. L. A. Turner with the above title, which appeared in the September number of the 'Philosophical Magazine.' In this paper Dr. Turner proposes an alteration of the assignment of principal quantum numbers to certain terms of atomic number greater than 28. My object is to show that his reasons for the change hardly seem adequate, and to point out an objection to his scheme of quantum numbers and some quantitative evidence which seems definitely to favour Bohr's assignment, and which has not, so far as I know, been pointed out before.

The principal facts are as follows:—We are concerned only with terms corresponding to orbits which penetrate into the core\*. For any atom, let  $q_0$  be the limiting quantum defect for a sequence of terms; we consider the values of  $q_0$  for corresponding sequences of such terms, of atoms of the same chemical subgroup in the same state of ionization (for example, the limiting quantum defects  $q_0$  of the  $s$  sequences of neutral Li, Na, K, Rb, Cs).

\* I use the nomenclature *core* and *series electron* for Dr. Turner's *kernel* and *valency electron*; *kernel* tends to be confused with the German *kern* (= nucleus); and in many cases (*e.g.* spectra of highly-ionized atoms) the term *valency electron* for the electron concerned in the emission of the optical series spectrum is somewhat a misnomer. Following Hicks, a set of terms corresponding to orbits with the same value of  $k$  but different values of  $n$  will be called a *sequence*. *Corresponding sequences* of different atoms are sequences with the same value of  $k$ .

If  $p$  is the number of the period in the periodic table to which the element belongs, then with Bohr's assignment of quantum numbers, such values of  $q_0$  are approximately linear in  $p$ , as pointed out by Prof. H. N. Russell\*, and in fact increase by nearly 1 (usually by rather less) for each increase of 1 in  $p$ . So that, if  $q_0$  is plotted against the atomic number  $N$ , the points lie approximately on a series of straight lines meeting one another at definite angles at points where the difference of  $N$  for unit difference of  $p$  changes from 8 to 18, or 18 to 32.

On the other hand, Dr. Turner shows that an assignment of quantum numbers can be found such that  $q_0$  is approximately linear in the atomic number  $N$ ; and he believes this result to be significant.

None of the linear relations are exact with either assignment of quantum numbers, and Dr. Turner agrees that the fit to his linear relations is no better than that to Russell's relations; so that no argument as to the significance of either assignment can be obtained from such considerations. He gives four reasons in support of his proposed change, as follows:—

- (1) It would be expected that the relation between the values of  $q_0$  and the atomic number  $N$  (for corresponding sequences of atoms of the same subgroup) would be represented by some "smooth" curve, rather than a curve made up of pieces of straight lines of different slope.
- (2) If there were breaks in the curve due to change of structure in the long periods of the periodic table, such a break would not be expected to occur at potassium (as it does with Bohr's quantum numbers), as the K atom must have one structure or the other, but not both.
- (3) If Bohr's quantum numbers were correct, the linear relation between  $q_0$  and  $N$  obtained by increasing the quantum numbers (and so the values of  $q$ ) for Rb and Cs by integers 1 and 2 respectively would be a remarkable coincidence.
- (4) Similar alterations give similar results for the different subgroups of the periodic table.

First, I would point out that a reason corresponding to (3) can be framed in support of Bohr's assignment of quantum numbers, viz. :—If Dr. Turner's quantum numbers

\* This observation of Prof. Russell's is quoted (expressed in a slightly different way from that which I have given it here) in a note to Dr. Turner's paper.

were correct, the linear relation between  $q_0$  and  $p$  obtained by decreasing the quantum numbers for Rb and Cs by integers 1 and 2 respectively would be a remarkable coincidence\*. Apart from an independent idea of the way in which  $q_0$  would be expected to vary with atomic number, such an argument cannot therefore be used in support of either assignment; and the same applies to Dr. Turner's fourth reason.

In connexion with his first reason for the assignment of quantum numbers, Dr. Turner gives no arguments in support of his expectation that the relation between  $q_0$  and  $N$  should be represented as a "smooth" curve†; perhaps this is taken as self-evident, but I propose to show that on Bohr's theory it is unjustified.

Before doing this, it may be as well to point out that the quantum defect for a given orbit of the series electron depends in no very simple way on the dimensions of the different groups of orbits in the core and on the numbers of electrons in them; so that when we consider different atoms in the same state of ionization, for which both dimensions of core orbits and number of electrons in them are different, it is not easy to see without quantitative investigation how the quantum defects for corresponding orbits of such atoms will be related. For this reason, ideas of how the quantum defect should vary with atomic number, which are based more or less on guesswork or on purely verbal arguments, may not be very reliable. Nevertheless it is possible to show without mathematics that the values of  $q_0$  given by Bohr's assignment of quantum numbers are consistent with his theory of the structure of the core, and that the facts do not demand the alteration of quantum numbers suggested by Dr. Turner. It is necessary to use one result based on a mathematical investigation—namely, that the smaller the dimensions of a group of core orbits, the smaller its contribution to the quantum defect‡.

It is easiest to take a definite example, and I will consider

\* The two "coincidences" are, of course, not independent: they are connected by the facts that (a) the numbers 8, 18, 32, which occur as the differences between atomic numbers of homologous elements, are nearly in the ratio of 1:2:4; (b) that  $q^0$  (Bohr's value) increases by nearly 1 from one such element to the next; and (c) that both linear relations are only approximate.

† It is perhaps as well to point out that, either for the elements of a subgroup or for all the elements,  $q_0$  is a function of a discontinuous variable  $N$ ; so that to speak of a "continuous" variation of  $q_0$  with  $N$  is meaningless. If  $q_0$  is plotted against  $N$  and a curve drawn through the points for a given subgroup, it must be remembered that apart from the plotted points this curve is purely diagrammatic, and that intermediate points on the curve have no physical significance.

‡ This result can easily be seen from some theoretical work which I have given elsewhere (Proc. Roy. Soc. vol. 106. p. 552 (1924)).

the  $s$  sequences of the alkali metals. From Li to K the difference of atomic number is 16, and the increase of  $q_0$  is nearly 2. From K to Rb the atomic number increases by 18; so, according to Dr. Turner, the limiting quantum defect would be expected to increase by about 2 again. This might perhaps be the case if the difference of structure between K and Rb were comparable to the difference of structure between Li and K; but this is not so, as shown by the fact that the difference of atomic number between K and Rb is 18 and not 16, and by the absence of an element with atomic number and properties intermediate between K and Rb corresponding to Na between Li and K.

By going into some details, we can deduce the direction in which the actual value of  $q_0$  for Rb should differ from the value extrapolated from the relation between  $q_0$  and  $N$  for Li, Na, and K.

The core of the Li atom consists of two orbits of principal quantum number  $n=1$ ; the core of the K atom consists, in addition, of 8 orbits with  $n=2$  which lie well outside\* the orbits with  $n=1$ , and a group of 8 orbits with  $n=3$  which similarly lie well outside the orbits with  $n=2$ .

Let us imagine an atom of the atomic number of Rb, whose difference in structure from the K atom is comparable to the difference between this and the Li atom; that is, imagine an atom with a core built up of an argon-like structure similar to the core of a K atom, with another group of electrons (say 9) *outside* it and a further group of electrons (say 9) *outside* that. I will call this a "pseudo-Rb" atom. We might perhaps expect that the relation between  $q_0$  and  $N$  for Li, Na, K, and pseudo-Rb would be represented by a smooth curve. But on Bohr's theory 10 of the 18 electrons which have to be added to the argon-like structure to give the core of the Rb atom are in orbits of the same principal quantum number, and so of the same dimensions, as some orbits already present. The consequence is that the dimensions both of the orbits of these 10 electrons, and of the orbits of the further 8 electrons, are smaller than they would be if all the 18 electrons were added in orbits outside the argon-like structure as in the case of pseudo-Rb. The result of this is that the quantum defect for any orbit of the series electron which penetrates into the core must be considerably smaller than it would be for pseudo-Rb;

\* Some of the orbits of the group of principal quantum number 2 penetrate into the region in which those of quantum number 1 move; in saying that one orbit lies "outside" another, I mean only that its time mean radius is greater.



*i. e.*, smaller than the quantum defect extrapolated from the relation between  $q_0$  and  $N$  for Li, Na, and K.

This is in complete agreement with observation, if Bohr's assignment of quantum numbers is adopted. On the other hand, if Dr. Turner's quantum numbers are adopted, the value of  $q_0$  for Rb lies somewhat *above* a reasonable smooth ( $q_0, N$ ) curve passing through the points for Li, Na, and K (the curve not being restricted to be a straight line).

Similar reasoning shows that the value of  $q_0$  for the  $s$  sequence of Cu must be *smaller* than the value obtained by extrapolating the relation between  $q_0$  and  $N$  for Li, Na, and K; this is the case if Bohr's quantum numbers are adopted, but Dr. Turner's quantum numbers bring the Cu point above the curve for the alkali metals.

Also, in contradiction to Dr. Turner's second reason for his assignment of quantum numbers, it appears, according to the above reasoning, that a break of the ( $q_0, N$ ) curve for the alkali metals would be expected just at potassium, since it is the element of the subgroup before and after which the process of building up the atom is different.

It seems, therefore, that the facts called by Dr. Turner in evidence of his proposed alteration of quantum numbers are in no way inconsistent with Bohr's theory of the core structure and his assignment of quantum numbers to orbits of the series electron. I will now turn to an objection to Dr. Turner's scheme, and some positive evidence in favour of Bohr's scheme.

The former can best be explained by an example. If for Cs the first  $s$  term of the optical spectrum corresponds to an  $8_1$  orbit (Dr. Turner's assignment) instead of a  $6_1$  orbit (Bohr's assignment), what are we to think of the  $6_1$  and  $7_1$  orbits, which must be more firmly bound than the  $8_1$ ? They cannot be possible orbits of the series electron, since the orbit corresponding to the first  $s$  term is the normal, and so most firmly bound, orbit of the series electron, as shown by the ready absorption of the principal series, and by the agreement of the ionization potential with the value of the term. If terms corresponding to the  $6_1$  and  $7_1$  (and  $6_2$  and  $7_2$ ) orbits do not appear in the optical spectrum, it must be because the core already contains electrons in these orbits; if so, terms corresponding to them would be expected to appear in the X-ray spectrum, and such terms would be expected to be quite fairly large for the heavier elements for which Dr. Turner's assignment of quantum numbers to orbits of the series electron demands  $9_1$  and  $10_1$  core orbits. Actually, if the usual classification of X-ray terms is accepted, P X-ray terms ( $n=6$ ) only

appear in the very heaviest elements, in accordance with Bohr's assignment of quantum numbers, and there seems no reason at all to upset this classification.

Finally, I will mention some positive evidence for Bohr's assignment of quantum numbers to orbits of the series electron.

The wave-numbers of the first *s* or *p* terms of the spectra of different elements of the same subgroup are not far different, the general (but not universal) tendency being for the wave-number to increase somewhat with decreasing atomic number; with Bohr's assignment the principal quantum number of the orbit in question increases by 1 from one period to the next. Examples are given in Table I.

TABLE I.—Orbits of Series Electrons.

Element.	N.	Orbit.	$\nu/R$ .
Cs .....	55	6 <sub>1</sub>	·286
Rb .....	37	5 <sub>1</sub>	·307
K .....	19	4 <sub>1</sub>	·319
Na .....	11	3 <sub>1</sub>	·376
Li .....	3	2 <sub>1</sub>	·396
Au .....	79	5 <sub>1</sub>	·679
Ag .....	47	4 <sub>1</sub>	·557
Cu .....	29	3 <sub>1</sub>	·568

Values for  $\nu/R$  from Fowler's 'Report on Series in Line Spectra,' except for Au, for which the term value is taken from a paper by Thorsen (*Naturwiss.* vol. xxvii. p. 501, 1923).

TABLE II.—Core Orbits.

Element.	N.	Orbit.	$\nu/R$ .	Orbit.	$\nu/R$ .
Th .....	90	5 <sub>1</sub>	19·8	5 <sub>2</sub>	about 11
Ce .....	58	4 <sub>1</sub>	21·7	4 <sub>2</sub>	15·8
Z .....	40	3 <sub>1</sub>	31·4	3 <sub>2</sub>	(25)
Pb .....	82	5 <sub>1</sub>	10·3	5 <sub>2</sub>	6·4
Sn .....	50	4 <sub>1</sub>	10·7	4 <sub>2</sub>	6·6
Ge .....	32	3 <sub>1</sub>	(12·9)	3 <sub>2</sub>	[9·0]
Au .....	79	5 <sub>1</sub>	7·8	5 <sub>2</sub>	8·3? [3·8]
Ag .....	47	4 <sub>1</sub>	7·5	4 <sub>2</sub>	3·3? [3·9]
Cu .....	29	3 <sub>1</sub>	(8·3)	3 <sub>2</sub>	5·2
Cs .....	55	5 <sub>1</sub>	(2·2)		
Rb .....	37	4 <sub>1</sub>	(2·4)		
K .....	19	3 <sub>1</sub>	(3·0)		
Na .....	11	2 <sub>1</sub>	(4·0)		

Values not bracketed have been taken from a paper by Coster (*Naturwiss.* vol. xxvii. p. 567); values in brackets have been obtained by reading off curves of  $\nu/R$  against *N*, given in diagrams in this paper—those in square brackets from interpolated parts, and those in round brackets from extrapolated parts of these curves. The value for the 5<sub>2</sub> orbit of Th is interpolated from Coster's table; the value  $\nu/R=17$  obtained by reading off the curve seems unlikely.

There is a corresponding relation between the X-ray spectra of such elements which I have not seen pointed out hitherto. If we consider terms corresponding to loosely-bound  $n_k$  core orbits of elements of the same subgroup, keeping  $k$  constant but increasing  $n$  by 1 on going from one period to the next, it is found that these terms also are not far different, and show a general tendency to increase with decreasing atomic number. Examples are given in Table II.

A mathematical analysis on the assumption of a central field shows that this correspondence is significant, and that if for elements of the same subgroup the values of the terms corresponding to loosely-bound core orbits with a given value of  $k$ , but values of  $n$  increasing by 1 from one period to the next, are nearly the same, then, if the orbits of the series electron for that value of  $k$  penetrate into the core, the value of  $q_0$  for them must increase by about 1 from one period to another of the periodic table.

Table II. shows that the values of such X-ray terms are in fact nearly the same, and the conclusion gives an almost decisive preference to Bohr's quantum numbers for the orbits of the series electron.

Further evidence is given by a detailed numerical analysis of the field of the atom from the observed terms of the optical and X-ray spectra on lines worked out independently by Fues\* and myself†. Fues (*loc. cit.* 4th paper) has shown that for Cs, assuming Bohr's quantum numbers, a central field can be found which will reproduce the observed terms of the optical and X-ray spectra with errors not much greater than those for Na,  $Mg^+$ , and  $Al^{++}$ . I have come independently to the same conclusion, and in fact have found it possible in the case of Rb and Cs to determine the atomic field approximately without making use of the  $s$  and  $p$  terms of the optical spectra; from the field so found, the quantum defects for these terms can be calculated, and most definitely confirm Bohr's assignment of quantum numbers, and not Dr. Turner's.

I conclude, therefore, that not only is there no demand for the alteration of quantum numbers suggested by Dr. Turner, but further that, at any rate in most cases, Bohr's quantum numbers for terms corresponding to those orbits which penetrate the core are definitely correct.

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Yours faithfully,  
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\* E. Fues, *Zeit. f. Phys.* vol. ii. p. 364, vol. xii. p. 1 (1922); vol. xiii. p. 211 (1924); vol. xxi. p. 265 (1924).

† D. R. Hartree, *Proc. Camb. Phil. Soc.* vol. xxi. p. 625 (1923).

XLI. *The Magnetic Rotary Dispersion of certain Paramagnetic Solutions.* By R. W. ROBERTS, M.Sc., Asst. Lecturer and Demonstrator in Physics, The University of Liverpool\*.

IN a previous paper† on this subject it was shown that, in solutions of cobalt sulphate and cobalt acetate in water, the cobalt atom is capable of producing a negative magnetic rotation. This rotation, although large relative to water, appeared only on the high-frequency side of the principal absorption-band which lies at the borders of the visible and ultraviolet. In an aqueous solution of cobalt chloride the rotation was nowhere negative, although from the form of the rotary-dispersion graph of this solution it was evident that, on the ultraviolet side of the absorption-band, the cobalt atom was exerting a negative rotation. In solutions of the corresponding salts of nickel, no trace of a negative rotation was apparent.

In view of these results, which do not seem to have a ready explanation on the modern theory of magneto-optics, it seemed worth while to continue the investigations with solutions of other cobalt and nickel salts. For the purpose of calculation, the refractive indices of these solutions in the visible and ultraviolet have also been determined, and an endeavour has been made to enter into a quantitative examination of the experimental results.

In the work previously published, owing to the lack of a suitable source of light, the rotation for only one wave-length could be found on the visible side of the absorption-band in the cobalt solutions. Using a mercury vacuum lamp, and by working with more dilute solutions, it was found that the rotary dispersion in the neighbourhood of the absorption-band was strongly anomalous.

The presence of anomalous rotary dispersion, as we here use the term, is not predicted by the usual magneto-optical theory based on the Hall effect, yet instances of absorption-bands exhibiting anomalous rotary dispersion are not wanting. Schmauss‡ found that anomalous rotary dispersion existed in alcoholic solutions of the aniline dyes; his results, however, were not confirmed by Bates§. Livens|| has shown

\* Communicated by Prof. L. R. Wilberforce, M.A.

† Richardson, Roberts, and Smith, *Phil. Mag.* xlv. p. 912 (1922).

‡ *Ann. d. Phys.* ii. p. 280 (1900).

§ *Ann. d. Phys.* xii. p. 1901 (1903).

|| *Phil. Mag.* xxvi. p. 362 (1913).

that Schmauss's results can be explained on the hypothesis of the Hall effect, when allowance is made for the polarization of the medium due to the electric force of the light wave. Schmauss\* has also found instances of anomalous rotary dispersion in liquid oxygen and in aqueous solutions of neodymium, praseodymium, and erbium nitrate. These results have been confirmed in part by the researches of G. J. Elias†, who found distinct examples of anomalous rotation in some solutions of the rare earths. Unmistakable evidences of anomalous rotary dispersion have been found by R. W. Wood‡ in an aqueous solution of praseodymium nitrate and in a solid film of neodymium nitrate. At the temperature of liquid air, J. Becquerel§ found the crystals tysonite and xenotime to possess anomalous rotation. It is noteworthy that in all the cases cited, with the exception of the alcoholic solutions of the aniline dyes, the substances are paramagnetic. It appears, therefore, that the study of the magnetic rotary dispersion in paramagnetic substances is capable of yielding information which cannot be obtained from the study of ordinary dispersion alone ||.

#### ROTARY DISPERSION FORMULÆ.

Most of the rotary dispersion formulæ have been based on the generalized Sellmeier formula,

$$n^2 = a_0 + \frac{a_1}{\lambda^2 - \lambda_1^2} + \frac{a_2}{\lambda^2 - \lambda_2^2} + \dots$$

A better basis would be the Lorenz-Lorentz formula,

$$\frac{n^2 - 1}{n^2 + 2} = a_0 + \frac{a_1}{\lambda^2 - \lambda_1^2} + \frac{a_2}{\lambda^2 - \lambda_2^2} + \dots$$

Certainly, in work on dispersion—particularly in the case of solutions—the Lorenz-Lorentz formula gives a far better representation of the experimental facts than the Sellmeier formula does. Using the Lorenz-Lorentz formula, an expression for the magnetic rotation of a substance may be easily derived. Larmor¶ has shown that, in the case

\* *Ann. d. Phys.* x. p. 853 (1903).

† *Ann. d. Phys.* xxxv. p. 299 (1913).

‡ *Phil. Mag.* ix. p. 725 (1905); xv. p. 270 (1908).

§ *Phil. Mag.* xvi. p. 153 (1908).

|| *Cf.* J. J. Thomson, *Phil. Mag.* xl. p. 713 (1920).

¶ *'Æther and Matter,'* p. 352.



of a substance whose vibrators are subjected to the Hall effect and have all the same value for  $\frac{e}{m}$ , the magnetic rotation  $\delta$  is given by the formula (of the Becquerel type),

$$\delta = -\frac{e}{2mc^2} \lambda \frac{dn}{d\lambda}, \quad . \quad . \quad . \quad . \quad (1)$$

where  $e$  is the electronic charge in electrostatic units.

The Lorentz formula may be written in the form \*

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} \sum \frac{e^2}{m(p_s^2-p^2)}, \quad . \quad . \quad . \quad . \quad (2)$$

in which symmetrical units are used as in (1) and the suffix to them has been dropped.

We have therefore

$$\frac{3}{n^2+2} = \text{const.} - \frac{e^2}{3\pi mc^2} \sum \frac{\lambda_s^4}{\lambda^2 - \lambda_s^2}. \quad . \quad . \quad . \quad (3)$$

Using (1) and (3), we obtain

$$\delta = \frac{e^3}{18\pi m^2 c^4} \cdot \frac{(n^2+2)^2}{n} \sum \frac{\lambda_s^4 \lambda^2}{(\lambda^2 - \lambda_s^2)^2}, \quad . \quad . \quad . \quad (4)$$

which is a simple deduction of the polarization formula obtained by Sir J. Larmor†, S. S. Richardson‡, and L. H. Siertsema§. For solutions we shall use (4) in the form

$$\frac{\delta \lambda^2 n}{(n^2+2)^2} = x \frac{\delta_w \lambda^2 n_w}{(n_w^2+2)^2} + \sum \frac{a_s}{(1 - \lambda^{-2} \lambda_s^2)^2}, \quad . \quad . \quad (5)$$

where  $n$ ,  $n_w$  are the refractive indices of the solution and solvent respectively, and  $\delta$ ,  $\delta_w$  the corresponding rotations:  $x$  is the number expressing the mass in gm. of solvent in 1 c.c. of the solution. The  $a_s$ 's are quantities involving electronic constants, and the  $\lambda_s$ 's are the characteristic wave-lengths of the solute. For colourless solutions, Heydweiller|| and his co-workers have shown that the natural dispersion in the visible and ultraviolet is controlled by a number of electrons belonging to the anion of the dissolved salt and a comparatively larger number of electrons of

\* O. W. Richardson, 'The Electron Theory of Matter,' p. 148.

† 'Æther and Matter,' p. 200.

‡ Phil. Mag. xxxi. p. 454 (1916).

§ Proc. Amst. Acad. xviii. 2, p. 925.

|| Ann. d. Phys. xli. p. 499 (1913); xliv. p. 977 (1914); xlix. p. 653 (1916).

much higher frequency. The free period of the anion electrons controlling the dispersion appears to be almost independent of the kation. For coloured solutions, one or more additional  $\lambda_s$ 's must be introduced.

If we form the difference

$$\Delta = \frac{\delta \lambda^2 n}{(n^2 + 2)^2} - x \frac{\delta_w \lambda^2 n_w}{(n_w^2 + 2)^2}$$

from the experimental results, we may take

$$\Delta = \sum \frac{a_s}{(1 - \lambda^{-2} \lambda_s^2)^2}$$

to be that additive quantity on the basis of the Hall effect hypothesis which is characteristic of the solute. The differences  $\Delta$  for the salts used in the present work have been plotted against  $\lambda^{-2}$  in fig. 6. It will be readily seen from the strong anomalous rotary dispersion at the absorption-bands, that the hypothesis of the Hall effect alone cannot explain the experimental results.

Drude\* has developed a formula on the hypothesis of molecular currents which predicts the possibility of anomalous rotary dispersion. It is most likely that in the paramagnetic liquids under consideration both the molecular currents and the Hall effect are operative. As a first approximation we shall consider only the molecular current effect, and on this hypothesis we shall obtain a further polarization formula. The following analysis is a modified form of that due to Drude, taking into account the force arising from the polarization of the medium, which force Drude neglects. Only the leading steps in the working are given, and for the sake of brevity and simplicity quaternion notation is used. Where the symbols are given without definition they are to be taken as having the meaning given by Drude.

Consider a plane polarized wave travelling in the direction of the magnetic field. Let this direction coincide with the  $z$  axis which is parallel to the unit vector  $k$ .

Maxwell's equations for the medium may be written

$$\frac{1}{c} \frac{\partial}{\partial t} (\mathbf{H} + \mathbf{V} \nabla \Sigma \xi_s \alpha_s) = -\mathbf{V} \nabla \mathbf{E}, \quad . \quad . \quad . \quad (6)$$

$$\frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \mathbf{V} \nabla \mathbf{H}, \quad . \quad . \quad . \quad (7)$$

where

$$\alpha_s = 4\pi \frac{N_s e q_s}{c \Gamma_s} k,$$

\* Drude, 'Theory of Optics,' p. 418.

and  $\xi_s$  is the displacement of the centre of the orbit of the revolving electron of type  $s$ .

The equation of motion of this centre is

$$m_s \ddot{\xi}_s = -k_s \xi_s + e \left( \mathbf{E} + \frac{4\pi}{3} \mathbf{P} \right).$$

If  $\xi_s \propto e^{ipt}$  we have, in the usual way,

$$\xi_s = \frac{e \mathbf{E}}{m_s(p_s^2 - p^2)} \cdot \frac{1}{1 - \frac{4\pi}{3} \sum \frac{e^2}{m_s(p_s^2 - p^2)}},$$

which, by eqn. (2), gives

$$\xi_s = \frac{(n^2 + 2)}{3} \frac{e \mathbf{E}}{m_s(p_s^2 - p^2)}.$$

Remembering that  $\nabla = k \frac{\partial}{\partial z}$ , and taking  $\mathbf{E} = \mathbf{E}_0 e^{ip(t - \frac{z}{v})}$  with  $Sk\mathbf{E}_0 = 0$ , we have, following the convenient procedure of Leigh Page\*, the two equations

$$\frac{\partial^2 \mathbf{E}_0}{\partial z^2} = 2 \frac{p}{v} C_p V k \frac{\partial \mathbf{E}_0}{\partial z} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and

$$\frac{2p}{v} \frac{\partial \mathbf{E}_0}{\partial z} = -C_p V k \frac{\partial^2 \mathbf{E}_0}{\partial z^2} + \frac{p^2}{v^2} C_p V k \mathbf{E}_0. \quad . \quad . \quad (9)$$

where

$$C_p = \frac{4\pi}{3c^2} (n^2 + 2) \cdot \sum N_s \frac{e^2 q_s}{m_s \Gamma_s} \frac{p}{p_s^2 - p^2},$$

which are obtained from (6) and (7) by eliminating  $\mathbf{H}$ , and separating out the real and imaginary parts.

Neglecting the square of  $C_p$ , we obtain

$$\begin{aligned} \frac{\partial \mathbf{E}_0}{\partial z} &= \frac{p}{2v} C_p V k \mathbf{E}_0 \\ &= \frac{2\pi}{3c^3} n(n^2 + 2) \sum N_s \frac{e^2 q_s}{m_s \Gamma_s} \frac{p^2}{p_s^2 - p^2} V k \mathbf{E}_0, \end{aligned}$$

which gives the rotation per cm.

$$\delta = \frac{2\pi}{3c^3} n(n^2 + 2) \cdot \sum N_s \frac{e^2 q_s}{m_s \Gamma_s} \frac{\lambda_s^2}{\lambda^2 - \lambda_s^2}.$$

\* 'An Introduction to Electrodynamics,' p. 128.

We shall use this equation in the form

$$\frac{\delta\lambda^2}{n(n^2+2)} = x \frac{\delta_w\lambda^2}{n_w(n_w^2+2)} + \sum \frac{\alpha_s}{1-\lambda^{-2}\lambda_s^2}, \quad (10)$$

where the  $\alpha_s$ 's are quantities involving electronic and orbital constants (for a given field), and the remaining symbols have the same meaning as in eqn. (5). Drude's formula (38) p. 431, is obtained from (10) by taking  $n^2+2=\text{constant}$ ,  $x=0$ , and  $\lambda_s=\lambda_1$  and 0.

Forming the difference

$$D = \frac{\delta\lambda^2}{n(n^2+2)} - x \frac{\delta_w\lambda^2}{n_w(n_w^2+2)},$$

which may be calculated from the experimental results, we obtain a quantity which is characteristic of the solute. The differences  $D$  for the salts used in the present work are given in graphical form in fig. 5. As with the  $\Delta$  differences, we get anomalous dispersion at the absorption-band with the  $D$  differences. The formula for the  $D$  difference is able, however, to account for this anomalous dispersion, not only qualitatively but, as we shall see later, quantitatively. The best dispersion formula is that which will enable us to calculate the position of the absorption-bands in the spectrum, and at the same time to be able to account for the dispersion with the minimum number of constants. For the cobalt solutions considered, we shall see later that equation (10) is able to give a good approximate value for the wave-length of the principal absorption-band and also a representation of the rotary dispersion graphs almost within the limits of experimental error. It may be mentioned in passing that S. S. Richardson\* has given a rotary dispersion formula with few constants by means of which the absorption-bands and rotary dispersion of certain diamagnetic liquids can be calculated with extremely good accuracy. The formula is based on the Hall effect hypothesis.

## EXPERIMENTAL.

### *Magnetic Rotation.*

The method was the same as that described briefly in the previous paper. Owing to the strong absorbing power of the solutions, exposures of ten to twelve minutes' duration were necessary. To keep the work within reasonable limits,

\* Phil. Mag. xxxi. p. 232 (1916).

the readings obtained from the pilot plates have all been used in the construction of the graphs. For very strong lines the actual settings of the analyser were determined which gave equality of illumination of the lines in the upper and lower spectra of the divided field. About a dozen exposures were made on each plate—the first, third, etc. giving “half-shades” with the field in one direction, the second, fourth, etc. with the field in the opposite direction. The distances of the lines at which the “half-shades” occur from some well-known line in the iron arc spectrum were determined, and by means of a calibration curve, which was found to fit all the spectrograms with good accuracy, the wave-lengths of the “half-shade” lines were obtained. A graph was drawn in which the setting of the analyser was plotted against the half-shade wave-length. In the upper half of this graph the points refer to the settings with the field in one direction, and in the lower half to those obtained with the field in the opposite direction. From this graph could be found the doubled rotation for any wave-length well within the extreme half-shade wave-lengths. When this method was adopted, the rotations for wave-lengths  $\cdot 4$ ,  $\cdot 38$ ,  $\cdot 36$ ,  $\cdot 34 \mu$ , etc. were found, and these rotations were used in the construction of the rotary dispersion graphs. From the dozen points provided by each pilot plate, the rotations for two of the above-mentioned wave-lengths were obtained. It was arranged that one of these wave-lengths was included in the range of “half-shade” wave-lengths taken in by the next pilot plate. The agreement between the rotations obtained from different plates for the common wave-lengths was good. As a further check on the accuracy of this procedure, the rotations for a few of the strongest lines in the vacuum arc mercury spectrum were observed for some of the solutions; and it will be seen from the graphs that the rotations obtained in this way are quite close to the curve determined by the above method. It is extremely important for work in the near ultraviolet that the solutions should be as clear and pure as possible. Although the presence of small traces of impurities does not affect the rotation appreciably, it does, to a marked degree, affect the absorption. This was particularly noticeable with several of the nickel solutions investigated. For these salts, there is only a very narrow transparent region in the ultraviolet on the short wave-length side of the absorption-band at  $\cdot 405 \mu^*$ . Repeated filtering in several

\* Houstoun, Proc. Roy. Soc. Edin. xxxi. p. 547 (1911).



cases gave a great improvement in the intensity of the spectrograms. To reduce the rotations to absolute measure, Rodger and Watson's value \* for Verdet's constant of water at 20° C. for the yellow sodium line, namely 0.01309 min. per cm.-gauss, was used. The water-curves in figs. 1-4 have been constructed from the ratio values for the rotation of some strong lines in the iron arc spectrum given by S. S. Richardson †, using the above-mentioned Verdet's constant and the results of a large number of observations of the rotation of water for the sodium line 5893 and the iron line 4958. The curve obtained in this way was checked by direct determinations of the rotations for the mercury lines 5461, 4358, and the iron line 3306.

For all the rotations the correction for the end plates of the cell containing the liquids under test has been made by calculation, on the assumption that the rotation of the end plates varied as  $\lambda^{-2}$ . This assumption is a sufficiently accurate one, especially so in the formation of the differences D and  $\Delta$ .

### *Refractive Indices.*

As far as the author is aware, the determination of the refractive indices in the ultraviolet of aqueous solutions of nickel and cobalt salts, with the exception of nickel chloride ‡, does not seem to have been made. In the visible spectrum, however, Limann § has determined the refractive indices of aqueous solutions of a few nickel and cobalt salts for the lines  $H_{\alpha}$ , Na 5893  $\mu$ ,  $H_{\beta}$ , and  $H_{\gamma}$ .

The refractive indices of the solutions used in the present work were determined very simply and rapidly in the following way. The ordinary glass lenses of a spectrometer were removed, and replaced by two achromatic quartz-fluorite combinations constructed by Hilger. A hollow prism with very nearly plane parallel quartz cover-plates was carefully levelled and fixed on to the table of the spectrometer. Instead of the eyepiece, a photographic plate-holder was screwed on to the end of the inner draw-tube of the telescope at right angles to its axis. The spectrometer was adjusted for parallel light by Schuster's method ||, using the iron arc as source and focussing the

\* Phil. Trans. A 186. p. 621 (1895).

† S. S. Richardson, Phil. Mag. xxxi. p. 232 (1916).

‡ Heydweiller u. Grube, Ann. d. Phys. xlix. p. 653 (1916).

§ Limann, Zeit. f. Phys. viii. p. 13 (1922).

|| Phil. Mag. [5] vii. p. 95.

iron lines  $\cdot 4046$  and  $\cdot 4068 \mu$  (mean line). The focussing was done on a plain glass plate with fine lines ruled with a diamond on the side of the plate which first received the light. While the adjustments were made, the lines were observed with an eyepiece which was allowed to rest on the plain glass plate. In this way the resulting ultra-violet spectrum was found to be quite sharp throughout the region to be investigated. Instead of the usual wedge covering the slit, a sliding diaphragm with two apertures was employed, which—at a later stage—was replaced by one with three apertures when I found that such diaphragms were in common use.

The prism was first filled with water whose temperature was taken by a thermometer to an accuracy of  $0^{\circ}\cdot 1$  C. With the slit exposed to the light of a cadmium spark passing through the upper aperture of the diaphragm, an exposure of one to two minutes was made. The resulting spectrum may be conveniently termed a “water” spectrum. After this exposure, the diaphragm was removed so that the light was cut off from the slit, while the prism was emptied and rinsed out several times with the solution under test. When filled with the solution, a “solution” spectrum was taken with the slit exposed to the light passing through the middle aperture. To make sure that the prism was not moved during the process of emptying and filling, a second “water” spectrum was taken using the lower aperture of the diaphragm. The lines of this spectrum were in every case found to be under the lines of the first “water” spectrum. To vary the conditions of the work somewhat, another set of spectra was obtained on the same plate with the prism in a different position. The spectra were carefully measured to an accuracy of  $1/800$  mm., and from the measurements the refractive indices of the solution were determined graphically.

Flatow\* has studied with great care the refractive indices of water in the visible and ultraviolet. From his results, by drawing refractive index-temperature graphs, I find the following refractive indices for water at  $13^{\circ}$  C. :—

$\lambda$ .	$n$ .	$\lambda$ .	$n$ .
$\cdot 2195$	$1\cdot 39934$	$\cdot 3404$	$1\cdot 35085$
$\cdot 2265$	$1\cdot 39307$	$\cdot 3612$	$1\cdot 34780$
$\cdot 2313$	$1\cdot 38929$	$\cdot 3944$	$1\cdot 34409$
$\cdot 2428$	$1\cdot 38152$	$\cdot 4416$	$1\cdot 34020$
$\cdot 2573$	$1\cdot 37391$	$\cdot 4678$	$1\cdot 33858$
$\cdot 2676$	$1\cdot 36950$	$\cdot 4800$	$1\cdot 33793$
$\cdot 2749$	$1\cdot 36685$	$\cdot 5339$	$1\cdot 33544$

\* *Ann. d. Phys.* xii. p. 85 (1903).

Using these values, a large-scale graph (with  $n$  plotted against  $\lambda$ ) was drawn in three parts with the aid of a curve-tracer. The parts of this graph were made to overlap as much as possible. By means of this graph, the refractive indices of water for any wave-length within the range could be readily determined.

Having determined the refractive indices for a number of known lines in the "water" spectrum, which were chosen so as to be as nearly equally spaced as possible, a graph was drawn with these refractive indices plotted against the scale-readings of the chosen lines. This graph was found to be very nearly linear. Since lines with the same scale-reading have the same refractive index, the refractive indices of the solution for any line in its spectrum could be obtained from the graph when the scale-reading of the line is known.

The refractive indices obtained from the various prism settings agreed well within the limits of experimental error. In the graphs, one unit in the fifth decimal place was represented by one-tenth of a tenth of an inch so that estimates of the fifth decimal place in the refractive index could be made. Most of the results agreed within 8 units in the fifth figure of decimals, and in many cases the agreement was better than this.

The results of the refractive index determinations are given in the form of two graphs. For the magnetic rotation work these results are given to the fourth decimal place. The recorded refractive indices have all been read off from the graphs prepared for figs. 7 & 8, and corrected for the temperature difference from the temperatures neighbouring  $13^{\circ}0$  C. to  $20^{\circ}0$  C. on the assumption that the correction would be the same as that for water. This is sufficiently accurate for the purpose of calculation in the magnetic work. The temperature varied only very slightly during the time the photographs were taken. The mean temperature has been recorded in each case.

Using water as the reference liquid, refractive indices not much higher than 1.39 can be determined. With the present dearth of refractive index determinations for pure liquids in the ultraviolet, some solutions whose refractive indices were in the neighbourhood of 1.40 could not be determined by this method.

In some cases the mercury arc was used as a source instead of the cadmium spark. With such an intense source, the best photographs were obtained by forming an image of the source in the prism. In this way only the central portions

of the lenses were used. Preliminary experiments showed that, for the range of refractive indices considered, the error due to the spreading of the lines on the plate arising from the want of achromatism of the camera lens was small.

### SOLUTIONS.

The concentrations of the solutions have been determined by electrolytic deposition of the metal (Ni or Co) from ammoniacal solutions. In the case of nickel chlorate and cobalt chlorate solutions, the deposits were excellent. These chlorates were obtained from Kahlbaum. The recorded densities refer to room temperature, at which temperature all the solutions were prepared.

For the cobalt nitrate solution the concentration has been taken from the tables given by Heydweiller\*. This was necessary owing to loss of the solution through accident.

### RESULTS.

#### Water.

In the formation of the D and  $\Delta$  differences the functions

$\frac{R_w \lambda^2}{n_w(n_w^2 + 2)}$  and  $\frac{R_w \lambda^2 n_w}{(n_w^2 + 2)^2}$  are repeatedly required.  $R_w$  is

Verdet's constant in minutes per cm.-gauss. The required values have in all cases been read off from graphs of these functions, constructed with the data given below. The values of  $n_w$  for 20°C. have been taken from Flatow's results.

$\lambda$ .	$R_w$ .	$\frac{R_w \lambda^2 \times 10^4}{n_w(n_w^2 + 2)}$ .	$\frac{R_w \lambda^2 n_w \times 10^4}{(n_w^2 + 2)^2}$ .
·5893	·0131	9·030	4·248
·4958	·0190	9·230	4·355
·4529	·0232	9·372	4·430
·4308	·0260	9·465	4·480
·4199	·0275	9·519	4·512
·4046	·0299	9·597	4·550
·3609	·0391 <sup>5</sup>	9·919	4·719
·3100	·0573	10·562	5·070

\* *Zeits. f. Anorg. u. Allg. Chem.* cxvi. p. 42 (1921).

*Cobalt Chlorate.* (Fig. 1.)

(i.) Strong solution: density =  $d = 1.355$  gm. per c.c.  
 $x = .875$ .

Obs.	$\lambda$ in $\mu$ .	$n_{20^\circ}$	$R_{(\text{obs.})}$	$R_{(\text{calc.})}$	$\delta R \times 10^4$ .
<i>a</i> .....	.5780	1.3911	.0143	.0143	ref.
<i>b</i> .....	.4358	1.3984	absorpt.	—	—
<i>c</i> .....	.4046	1.4010	.0231	.0231	ref.
<i>d</i> .....	.3714	1.4044	.0295	.0295	0
<i>e</i> .....	.3664	1.4051	.0307	.0307	ref.
<i>f</i> .....	.3592	1.4060	.0325	.0323	+2
<i>g</i> .....	.3342	1.4095	.0391	.0393	-2

The absorption of this solution in the neighbourhood of the absorption-band at  $.510 \mu$  was so strong that, using a powerful mercury arc, no observations could be made for the strong lines  $.5461$  and  $.4358 \mu$ . With the exception of (*a*), the magnetic observations were obtained photographically. The ultraviolet refractive indices have been obtained by extrapolation from the results of visual observations with a Pulfrich refractometer on the mercury lines  $.5780$  (mean line),  $.5461$ ,  $.4358$ , and  $.4046 \mu$ .

If we try to represent the dispersion by means of a two-constant formula for the D difference, we find that, from observations (*a*) and (*c*),  $\lambda_1 = .448 \mu$ , and from (*c*) and (*e*),  $\lambda_1 = 1.239 \mu$ .

This indicates that the effect of the high-frequency electrons has been omitted. Providing for these, we take

$$D = \frac{a_1}{1 - \lambda^{-2} \lambda_1^2} + a_2.$$

From (*ace*)  $\lambda_1 = .499 \mu$ , which, considering the simple assumptions which have been made, is a fair approximation to the value  $\lambda = .510 \mu$  given by Houstoun for the position of the principal absorption-band. With the value  $\lambda = .499 \mu$  we find

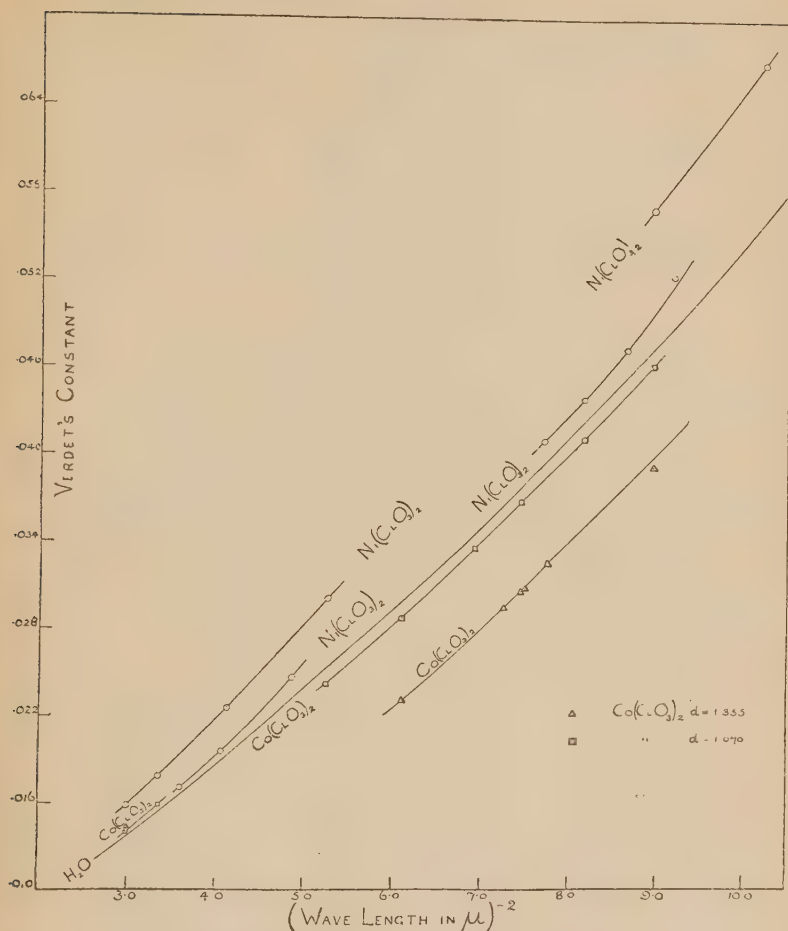
$$a_1 = +4.07 \times 10^{-5},$$

$$a_2 = -7.93 \times 10^{-5}.$$

Using these values, it will be seen that the Verdet's constants calculated from the formula are close to the observed ones.



Fig. 1.



(ii.) Weak solution:  $d = 1.070$  gm. per c.c.,  $x = .978$ .

Obs.	$\lambda$ in $\mu$ .	$n_{20}$ .	$R_{(\text{obs.})}$ .	$R_{(\text{calc.})}$ .	$\delta R \times 10^4$ .
a .....	.5780	1.3446	.0140	.0138	+2
b .....	.5461	1.3458	.0159	.0159	ref.
c .....	.4358	1.3516	.0242	.0242	ref.
d .....	.4046	1.3541	.0288	.0290	-2
e .....	.3800	1.3569	.0336	.0337	-1
f .....	.3664	1.3588	.0368	.0368	ref.
g .....	.3500	1.3612	.0410	.0411	-0
h .....	.3342	1.3640	.0462	.0461	+1

As with the strong solution, the position of the absorption-band cannot be calculated from a two-constant formula.

Taking the formula

$$D = \frac{a_1}{1 - \lambda^{-2} \lambda_1^2} + a_2,$$

we find from (acf),  $\lambda_1 = .517 \mu$ ,

(bcf),  $\lambda_1 = .507 \mu$ .

Using the latter value for  $\lambda_1$ , we obtain

$$a_1 = +6.7 \times 10^{-6},$$

$$a_2 = -1.36 \times 10^{-5}.$$

With these values we find good agreement between the calculated and observed values of R.

It will be observed that with both solutions of  $\text{Co}(\text{ClO}_3)_2$  we have the appearance of a negative constant. Such constants have been attributed to the existence of positive electrons. On Drude's theory, the presence of the negative constants means that the high-frequency electrons contribute to the paramagnetism of the solution.

*Cobalt Bromide.* (Fig. 2.)

$d = 1.100$  gm. per c.c.,  $x = .990$ .

Obs.	$\lambda$ in $\mu$ .	$n_{20^\circ}$	$R_{(\text{obs.})}$	$R_{(\text{calc.})}$	$\delta R \times 10^4$ .
<i>a</i> .....	.5893	1.3520	.0151	.0149	+2
<i>b</i> .....	.5780	1.3525	.0158	.0156	+2
<i>c</i> .....	.5461	1.3538	.0181	.0182	ref.
<i>d</i> .....	.4264	1.3613	.0289	.0289	ref.
<i>e</i> .....	.4082	1.3631	.0322 <sup>5</sup>	.0322	0 <sup>5</sup>
<i>f</i> .....	.3922	1.3648	.0356	.0356	0
<i>g</i> .....	.3780	1.3666	.0390 <sup>5</sup>	.0390 <sup>5</sup>	0
<i>h</i> .....	.3651	1.3685	.0426 <sup>5</sup>	.0426 <sup>5</sup>	ref.
<i>i</i> .....	.3535	1.3704	.0467	.0467	0

It is clear from the form of the D graph that a two-constant formula cannot account for the rotary dispersion in this solution. Assuming  $D = \frac{a_1}{1 - \lambda^{-2} \lambda_1^2} + a_2$ , we find  $\lambda_1 = .465 \mu$ . The low value for the principal absorption-band indicates the existence of another band in the ultra-violet. The wave-length of this absorption-band may be calculated approximately if we assume  $\lambda_1 = .510 \mu$ .

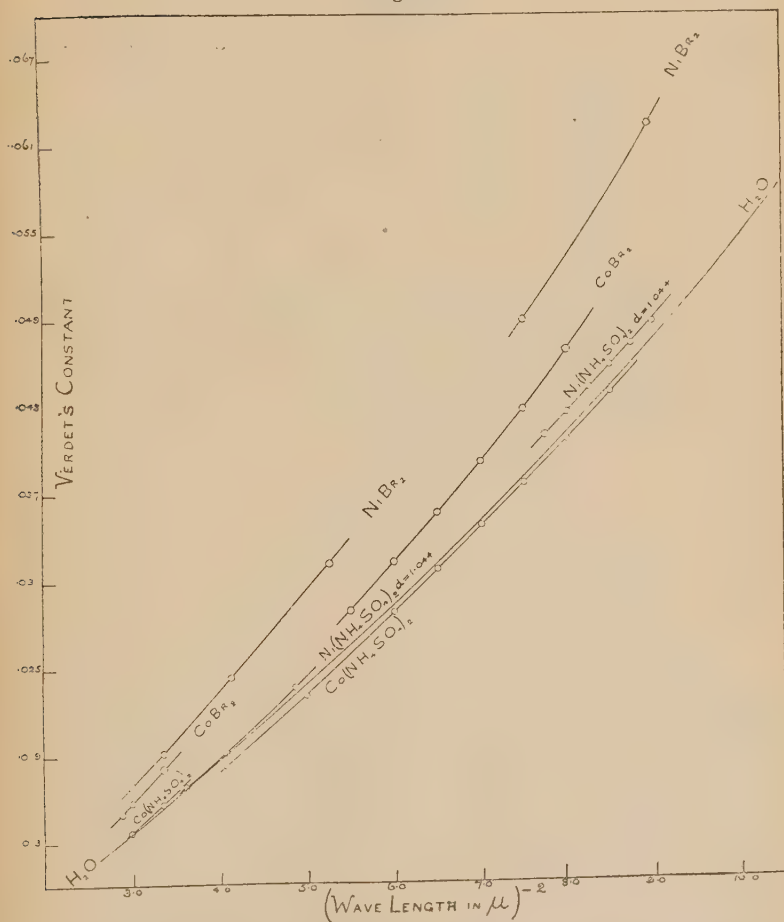
In this way we find

$$D = \frac{a_1}{1 - \lambda^{-2} \lambda_1^2} + \frac{a_2}{1 - \lambda^{-2} \lambda_2^2},$$

with

$$\begin{aligned} \lambda_1 &= .510 \mu, & \lambda_2 &= .246 \mu, \\ a_1 &= +9.7 \times 10^{-6}, & a_2 &= +5.65 \times 10^{-5}. \end{aligned}$$

Fig. 2.



With this formula the values of  $R$  have been calculated. The position of the ultraviolet absorption-band seems satisfactory, judging from the absorption-curve given by Houstoun for a solution of  $\text{CoBr}_2$ . The value for  $\lambda_2$  must

be taken as an effective one only. Houston records an absorption-band at  $\cdot 285 \mu$ . According to Lübben\*, the characteristic wave-length of the bromine anion is at  $\cdot 186 \mu$  in colourless solutions.

*Cobalt Nitrate.* (Fig. 3.)

$$d = 1\cdot078 \text{ gm. per c.c., } x = \cdot 980.$$

Obs.	$\lambda$ in $\mu$ .	$n_{20}$ .	$R_{(\text{obs.})}$ .	$R_{(\text{calc.})}$ .	$\delta R \times 10^4$ .
<i>a</i> .....	$\cdot 5893$	$1\cdot3572$	$\cdot 0128$	$\cdot 0128$	ref.
<i>b</i> .....	$\cdot 4200$	$1\cdot3620$	$\cdot 0242$	$\cdot 0242$	ref.
<i>c</i> .....	$\cdot 4000$	$1\cdot3639$	$\cdot 0278$	$\cdot 0277$	+1
<i>d</i> .....	$\cdot 3800$	$1\cdot3663$	$\cdot 0317$	$\cdot 0317$	ref.
<i>e</i> .....	$\cdot 3600$	$1\cdot3692$	$\cdot 0364$	$\cdot 0363$	+1
<i>f</i> .....	$\cdot 3500$	$1\cdot3705$	$\cdot 0394$	$\cdot 0390$	+4

With this solution, which was investigated before I had access to a mercury lamp, the rotation for only one line on the low-frequency side of the absorption-band could be determined. It is obvious from the difference graph that a two-constant formula cannot represent the dispersion. Introducing an extra constant, we find from

$$(abd), \quad \lambda_1 = \cdot 471 \mu,$$

$$(ace), \quad \lambda_1 = \cdot 468 \mu,$$

$$(bce), \quad \lambda_1 = \cdot 411 \mu,$$

with

$$D = \frac{a_1}{1 - \lambda^{-2} \lambda_1^2} + a_2.$$

This progression is undoubtedly due to the presence of another free period in the ultraviolet. The formula does not give a value for this free period, probably owing to the comparatively large negative value of the constant  $a_2$ . Using the first of the above values for  $\lambda_1$ , we find

$$a_1 = +1\cdot36^5 \times 10^{-5},$$

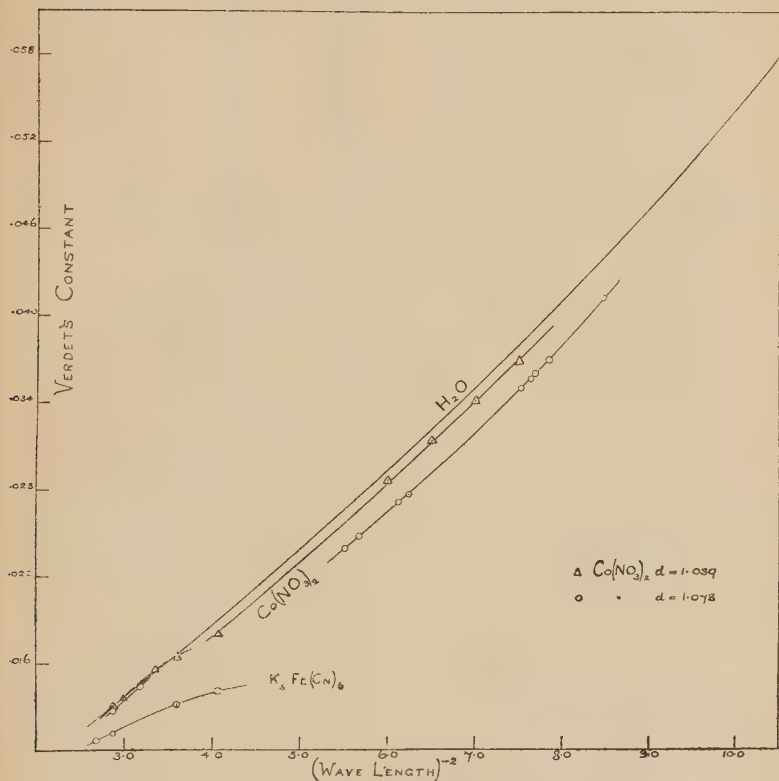
$$a_2 = -6\cdot64 \times 10^{-5}.$$

Even with this small value of  $\lambda_1$ , the agreement between the calculated and observed values of  $R$  is satisfactory.

\* *Ann. d. Phys.* xliv. p. 977 (1914).

The magnetic rotation in cobalt nitrate is interesting, as we find a negative value for  $D$  on the low-frequency side of the absorption-band. Ingersoll\*, who has investigated the magnetic rotary dispersion of a number of nickel and cobalt salts in the near infra-red, finds this negative difference to persist as far into the infra-red as he was able

Fig. 3.



to extend his observations. Wachsmuth† also gives the rotation of an aqueous solution of  $\text{Co}(\text{NO}_3)_2$  to be less than that of water, the two rotations referring to the yellow sodium line. I intend to make a more complete investigation of solutions of  $\text{Co}(\text{NO}_3)_2$  shortly.

\* Journ. Opt. Soc. Amer. vi. (Sept. 1922).

† Wied. Ann. xlv. p. 377 (1891).



$d=1.050$  gm. per c.c.,  $x=.983$ .

Obs.	$\lambda$ .	$n_{20}$ .	$R_{(obs.)}$ .	$R_{(calc.)}$ .	$\delta R \times 10^4$ .
<i>a</i> .....	5780	1.3439	.0136	.0143	-7
<i>b</i> .....	5461	1.3450	.0156 <sup>5</sup>	.0166	-9 <sup>5</sup>
<i>c</i> .....	5270	1.3458	.0169	absorpt.	
<i>d</i> .....	4958	1.3472	.0184	absorpt.	
<i>e</i> .....	4472	1.3502	.0230	.0230	0
<i>f</i> .....	4082	1.3534	.0288	.0288	0
<i>g</i> .....	3922	1.3550	.0317	.0317	0
<i>h</i> .....	3780	1.3566	.0347	.0346	+1
<i>i</i> .....	3651	1.3582	.0376	.0377	-1
<i>j</i> .....	3535	1.3597	.0406	.0408	-2
<i>k</i> .....	3430	1.3614	.0439	.0439	0

If we try a three-constant formula for D we find from

$$(aef), \quad \lambda_1 = .467 \mu,$$

$$(ehk), \quad \lambda_1 = .460 \mu,$$

$$(beh), \quad \lambda_1 = .480 \mu.$$

Attributing this low value of  $\lambda_1$  to the existence of another ultraviolet free period, and proceeding to calculate the corresponding wave-length  $\lambda_2$ , we find  $\lambda_2 = .510 = \lambda_1$ . This means that for this solution a two-constant formula

$$D \equiv \frac{a_1}{1 - \lambda^{-2} \lambda_1^2}$$

is sufficient to account for the rotary dispersion.

Assuming  $\lambda_1 = .510 \mu$ , I find

$$a_1 = +9.4 \times 10^{-6}.$$

It thus appears that the rotary dispersion in  $\text{Co}(\text{NH}_4\text{SO}_4)_2$  is conditioned almost entirely by a single free period corresponding to  $\lambda_1 = .510 \mu$ , the dispersive effect due to the ammonium sulphate radicle being almost nil. This statement seems to receive support from the behaviour of the refractive-index graph of this solution.

*Nickel Solutions.**Nickel Bromide.* (Fig. 2.) $d=1.110$  gm. per c.c.,  $x=.977$ .

Obs.	$\lambda$ in $\mu$ .	$n_{20}$ .	$R_{(obs.)}$ .	$R_{(calc.)}$ .	$\delta R \times 10^4$ .
<i>a</i> .....	.5780	1.3550	.0169	.0169	0
<i>b</i> .....	.5461	1.3569	.0192	ref.	—
<i>c</i> .....	.4916	1.3599	.0241	.0243	—2
<i>d</i> .....	.4358	1.3641	.0322	ref.	—
<i>e</i> .....	.3652	1.3721	.0488 <sup>5</sup>	ref.	—
<i>f</i> .....	.3342	1.3776	.0623	.0618	+5

The rotations for the first three lines have been determined visually, and for the last three photographically. Owing to the small region of transmission in the ultraviolet, the rotation for the two ultraviolet lines .3652  $\mu$  and .3342  $\mu$  cannot be determined with as great an accuracy as is possible with the cobalt solutions. To reduce the time of exposure within reasonable limits the angle of half-shade must be increased, thereby losing sharpness of contrast between the parts of the divided field.

From the D curve, is seen the existence of slight anomalous dispersion at the band  $\lambda=.405 \mu$ . If we include a term to represent this band, we find

$$\lambda_1 = .405 \mu, \quad \lambda_2 = .215 \mu,$$

$$a_1 = +1.44 \times 10^{-6}, \quad a_2 = +1.732 \times 10^{-4}.$$

It will be seen that the formula  $D = \frac{a_1}{1 - \lambda^{-2} \lambda_1^2} + \frac{a_2}{1 + \lambda^{-2} \lambda_2^2}$  gives values of R which are quite close to the observed values.

*Nickel Chlorate.* (Fig. 1.) $d=1.229$  gm. per c.c.,  $x=.925$ .

Obs.	$\lambda$ in $\mu$ .	$n_{20}$ .	$R_{(obs.)}$ .	$R_{(calc.)}$ .	$\delta R \times 10^4$ .
<i>a</i> .....	.5780	1.3713	.0159	.0154	+5
<i>b</i> .....	.5461	1.3723	.0179	.0179	ref.
<i>c</i> .....	.4916	1.3750	.0226	.0226	0
<i>d</i> .....	.4358	1.3789	.0301	.0301	ref.
<i>e</i> .....	.3342	1.3919	.0569	.0569	ref.
<i>f</i> .....	.3128	1.3967	.0674	.0683	—9

As with the nickel-bromide solution, a three-constant formula for  $D$  does not give a possible value for  $\lambda_1$ . Assuming  $\lambda_1 = .405 \mu$ , we find  $\lambda_2 = .216 \mu$ ,

giving  $a_1 = 2.8 \times 10^{-6}$ ,  $a_2 = 1.276 \times 10^{-4}$ .

A less concentrated solution also showed anomalous dispersion at the principal absorption-band (see figs. 1 & 5).

*Nickel Ammonium Sulphate.* (Fig. 2.)

The differences for this solution were too small to admit of computation. The observed Verdet's constants are given in graphical form.

For the sake of convenience, the values of  $a_1$  and  $a_2$  have been collected along with the ratios  $\frac{a_1}{c}$  and  $\frac{a_2}{c}$ , where  $c$  is the concentration of the salt in gm. per c.c. of solution.

	$c$ .	$a_1 \times 10^4$ .	$a_2 \times 10^4$ .	$\frac{a_1}{c} \times 10^4$ .	$\frac{a_2}{c} \times 10^4$ .
Co(ClO <sub>3</sub> ) <sub>2</sub> (i.) ...	.480	+ .407	- .793	+ .85	- .165
(ii.) ...	.092	+ .067	- .136	+ .73	- .15
CoBr <sub>2</sub> .....	.110	+ .097	+ .565	+ .88	+ 5.14
Co(NO <sub>3</sub> ) <sub>2</sub> .....	.098	+ .136	- .664	+ 1.39	- 6.78
NiBr <sub>2</sub> .....	.133	+ .014	+ 1.732	+ .11	+ 13.02
Ni(ClO <sub>3</sub> ) <sub>2</sub> .....	.304	+ .028	+ 1.276	+ .10	+ 4.20

It will be seen that, for the cobalt salts, the ratio  $\frac{a_1}{c}$  is of the same order of magnitude and about 8 times greater than the ratio for the nickel salts. Owing to this comparatively small ratio for the nickel salts, the dispersion in the nickel solutions is controlled almost entirely by the ultraviolet free periods. The ratio  $\frac{a_2}{c}$  varies in sign as well as magnitude. This is to be expected from the different meanings which have been attributed to  $a_2$  in the different salts.

*Miscellaneous Solutions.*

The striking difference between the magnetic properties of potassium ferrocyanide and potassium ferricyanide encouraged the author to carry out some observations on the magnetic rotary dispersion of solutions of these salts in

water. About a year after I had completed the observations on these solutions, I found from the references in Ingersoll's paper that Siertsema\* had studied the magnetic rotary dispersion in an aqueous solution of potassium ferricyanide. The following table gives the author's results.

*Potassium Ferricyanide.* (Fig. 3.)

$d=1.008$  gm. per c.c.,  $x=.991$ .

Obs.	$\lambda$ in $\mu$ .	$n_{20}$ .	$R_{(\text{obs.})}$ .	$R_{(\text{calc.})}$ .	$\delta R \times 10^4$ .
<i>a</i> .....	.6104	1.3353	.0107	.0105	+2
<i>b</i> .....	.5893	1.3360	.0112	.0112	ref.
<i>c</i> .....	.5270	1.3362	.0132	.0133	-1
<i>d</i> .....	.4958	1.3393	.0141	.0141	ref.

The line  $.6104 \mu$  was obtained by feeding the iron arc with lithium chloride. The observations on this line could not be made easily. No observations could be made on the apparently strong lithium line  $.6708 \mu$ .

The rotary dispersion curve obtained from a large number of observations on the lines tabulated above was so striking that it was suspected that changes had occurred in the solution while the observations were in progress. To ascertain if this was or was not the cause of the variation, another solution of almost the same concentration was prepared, and the observations taken in the reverse order. It was found that the curve given by this second solution was parallel to and above (corresponding to the smaller concentration of this solution) the original curve. The difference between the two curves is too small to be shown easily on fig. 3.

Taking the rotations for the lines  $.5893 \mu$  and  $.4958 \mu$  to be the more reliable, we find that with  $D = \frac{a_1}{1 - \lambda^{-2} \lambda_1^2}$ ,  $\lambda_1 = .427 \mu$ , which does not seem an unreasonable value for the position of the absorption-band.

This value for  $\lambda_1$  gives

$$a_1 = -6.04 \times 10^{-5}.$$

The rotations calculated for the lines  $.6104 \mu$  and  $.5270 \mu$  are not far from the observed values. A three-constant formula for  $D$  does not give a likely value for  $\lambda_1$ .

According to these results it is seen that the rotary dispersion in potassium ferricyanide is in accordance with Drude's molecular-current theory. As with  $\text{Co}(\text{ClO}_3)_2$  and

\* *Arch. Néer.* (2) v. p. 447 (1900).

$\text{Co}(\text{NO}_3)_2$ , the negative rotation of  $\text{K}_3\text{Fe}(\text{CN})_6$  arises from the electrons which contribute to the paramagnetism of the solution.

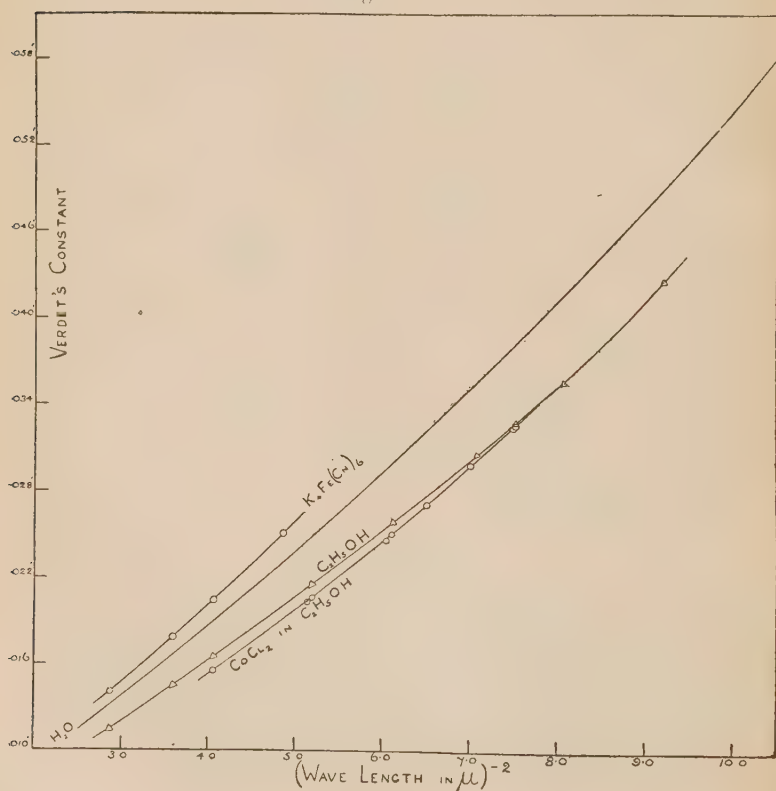
Siertsema states that the rotary dispersion in  $\text{K}_3\text{Fe}(\text{CN})_6$  is greater than the inverse fourth power of the wave-length. The above formula for  $D$  also gives the same result.

*Potassium Ferrocyanide.* (Fig. 4.)

$$d = 1.076^5 \text{ gm. per c.c., } \alpha = .957.$$

Obs.	$\lambda$	$n_{20}$	R.	$R_{\text{calc.}(5)}$	$R_{\text{calc.}(10)}$
a .....	.5893	1.3559	.0140	.0140	.0140
b .....	.5270	1.3585	.0178	.0178	.0178
c .....	.4958	1.3602	.0205	.0205	.0205
d .....	.4529	1.3631	.0251	.0251	.0251
e .....	.4406	1.3641	.0266	.0267	.0267

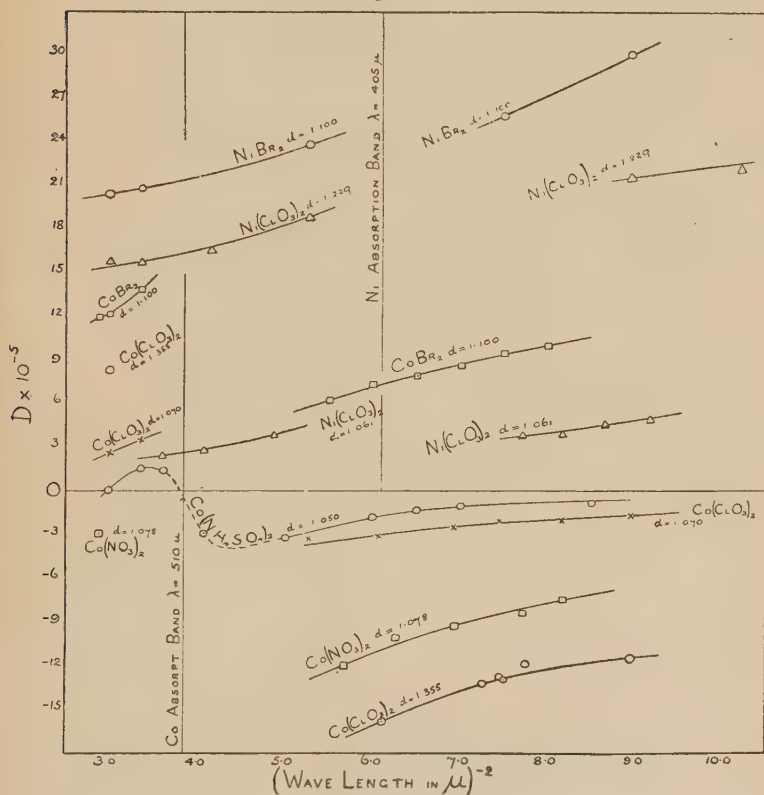
Fig. 4.





The rotary-dispersion curve of this solution follows the usual trend of such curves for diamagnetic substances. The rotations for the last two lines were obtained photographically. For this solution we can apply either equation (5) or equation (10) to calculate the rotary dispersion.

Fig. 5.



From equation (5) we obtain

$$a_1 = +3.51 \times 10^{-5}, \quad \lambda_1 = .170 \mu.$$

Equation (10) gives

$$a_1 = +5.98 \times 10^{-5}, \quad \lambda_1 = .237 \mu,$$

where, in both cases, a two-constant formula has been used for the differences  $\Delta$  and  $D$ . The agreement between the values of the rotations calculated from (5) and (10) and the observed values is quite satisfactory. The decision as to

Fig. 6.

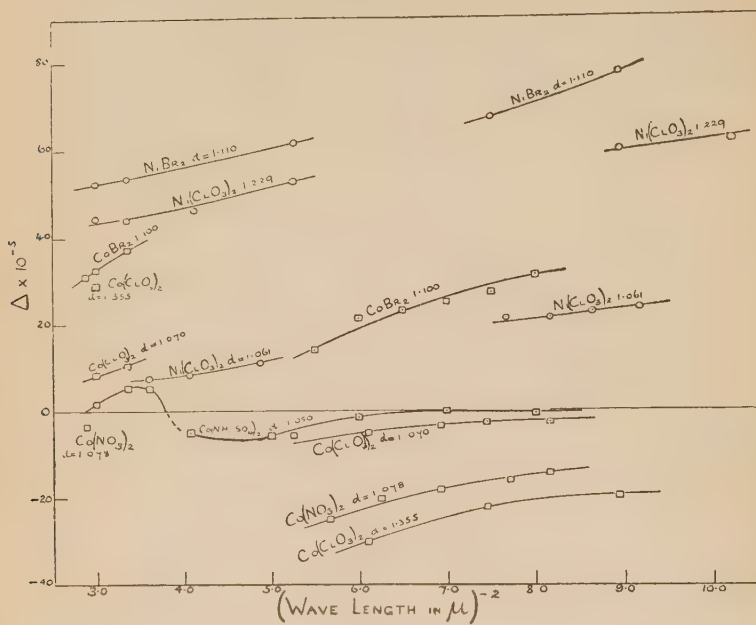
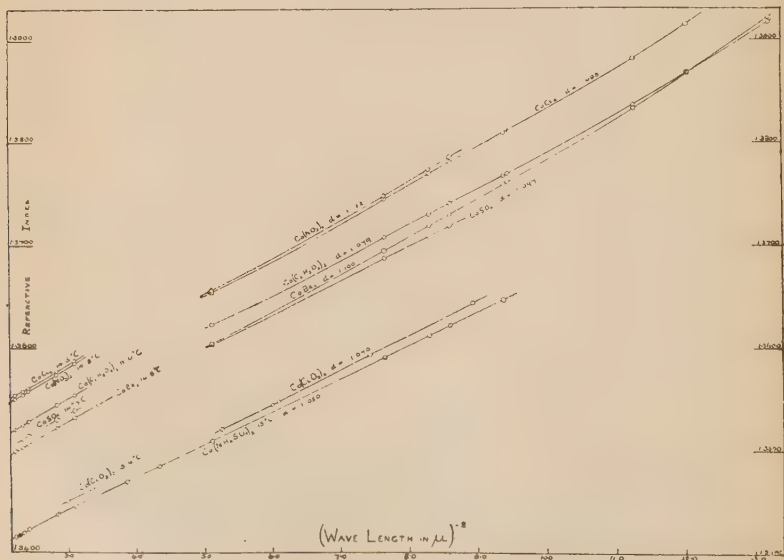


Fig. 7.





## SUMMARY.

1. The aqueous solutions of cobalt and nickel salts investigated show anomalous rotary dispersion at their principal absorption-bands. This anomalous rotary dispersion is much stronger for the cobalt solutions than for the nickel solutions.

2. The high-frequency electrons in cobalt solutions, as well as in  $K_3Fe(CN)_6$ , give rise to the negative rotation displayed by these salts.

3. The rotary dispersion in the solutions investigated may be calculated from the formula

$$\frac{\delta\lambda^2}{n(n^2+2)} = x \frac{\delta_w\lambda^2}{n_w(n_w^2+2)} + \sum \frac{a_s}{1-\lambda^{-2}\lambda_s^2},$$

which is derived from Drude's molecular current hypothesis by taking into account the electric polarization of the liquids.

I desire to express my best thanks to Prof. Wilberforce for the interest he has taken in the experiments and for the facilities and apparatus placed at my disposal; to Dr. S. S. Richardson for the interest he has taken in the work and his helpful criticism of the paper; to Mr. W. L. Marshall, B.Sc., and Mr. J. Smith, M.Sc., for assistance in the graphical and electrolytic work.

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University of Liverpool.

XLII. *On the Principle of Huygens.* By W. ANDERSON, B.Sc., Lecturer in Physics, The College of Technology, Manchester\*.

AN expression for the light disturbance  $s_0$  at a point O, in terms of the values of  $s$  over a closed surface S surrounding O, has been given by Kirchhoff †, viz.

$$4\pi s_0 = \int \left( \frac{\partial}{\partial r} \frac{s(t - \frac{r}{v})}{r} \cos(nr) - \frac{1}{r} \frac{\partial}{\partial n} s(t - \frac{r}{v}) \right) dS, \quad (1)$$

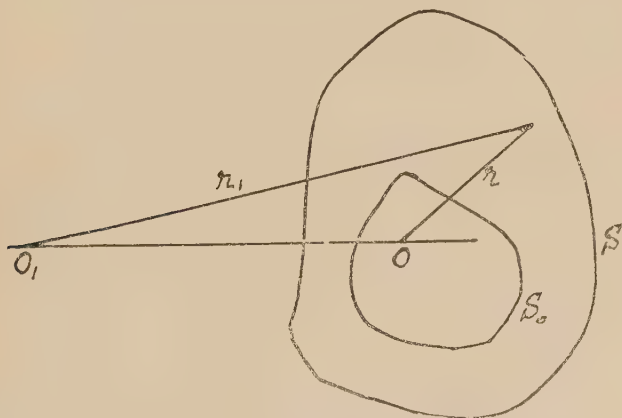
where  $r$  is the distance of  $dS$  from O,  $n$  is the normal to  $dS$  drawn inwards, and  $s(t - \frac{r}{v})$  is what  $s$  becomes when  $t - \frac{r}{v}$  is substituted in it for  $t$ .

\* Communicated by the Author.

† Wied. Ann. xviii. (1883).

It has been remarked by Larmor\* that the usual modes † of deriving this general formula are “not free from analytical complexity.” Since in the consideration of a number of diffraction problems it is sufficient to take the primary light wave as being completely given by  $s = \frac{1}{r} f\left(t - \frac{r}{v}\right)$ , the following derivation of (1) for this particular case may be of interest.

Let  $O_1$  be a point source emitting a disturbance given by  $s = \frac{1}{r_1} f\left(t - \frac{r_1}{v}\right)$  at points distant  $r_1$  from  $O_1$ . If  $O$  is a point distant  $a$  from  $O_1$ , and  $S$  is a closed surface enclosing  $O$ ,  $O_1$  being outside  $S$ , the disturbance at  $O$  will be  $s_0 = \frac{1}{a} f\left(t - \frac{a}{v}\right)$  and we wish to express  $s_0$  as an integral over  $S$ .



If  $F$  is a function of  $r_1$  and  $r$ , the distances of any point from  $O_1$  and  $O$ , and if  $\frac{dF}{dr_1}$  denotes the whole rate of variation of  $F$  with  $r_1$  along  $r_1$ , we have

$$\frac{dF}{dr_1} = \frac{\partial F}{\partial r_1} + \frac{\partial F}{\partial r} \cdot \frac{dr}{dr_1} \quad \dots \quad (2)$$

If  $G$  is another function of  $r_1$  and  $r$ , and  $\frac{dG}{dr}$  is the whole rate of variation of  $G$  with  $r$  along  $r$ , we also have

$$\frac{dG}{dr} = \frac{\partial G}{\partial r} + \frac{\partial G}{\partial r_1} \cdot \frac{dr_1}{dr} \quad \dots \quad (3)$$

\* Proc. L. M. S. ser. 2, i. p. 2 (1904).

† Drude, 'Theory of Optics,' Eng. ed. p. 169 (1902). Preston, 'Theory of Light,' 4th ed. p. 75 (1912).



Then it is easily seen geometrically that

$$\frac{dr}{dr_1} = \cos(r_1 r) = \frac{dr_1}{dr}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where  $\frac{dr}{dr_1}$  and  $\frac{dr_1}{dr}$  have the same meanings as in (2) and (3).

Now if  $dv$  denotes an element of volume, and  $d\omega$  an elementary solid angle with vertex at  $O_1$ , the value of  $\int \frac{1}{r_1^2} \frac{dF}{dr_1} dv$  taken through the whole space enclosed by  $S$  will be

$$\begin{aligned} \int \frac{1}{r_1^2} \frac{dF}{dr_1} dv &= \iint \frac{1}{r_1^2} \frac{dF}{dr_1} r_1^2 d\omega dr_1 \\ &= \int d\omega \int \frac{dF}{dr_1} \cdot dr_1 \\ &= \int \frac{dS \cos(nr_1)}{r_1^2} \cdot F, \end{aligned}$$

the normal  $n$  to  $dS$  being drawn outwards. If  $S_0$  is another surface enclosing  $O$ , and entirely inside  $S$ , the value of the above integral taken through the space between  $S_0$  and  $S$  will be

$$\int \frac{1}{r_1^2} \frac{dF}{dr_1} dv = \int \frac{F \cos(nr_1)}{r_1^2} dS - \int \frac{F \cos(nr_1)}{r_1^2} dS_0. \quad (5)$$

In the same way we get

$$\int \frac{1}{r^2} \frac{dG}{dr} dv = \int \frac{G \cos(nr)}{r^2} dS - \int \frac{G \cos(nr)}{r^2} dS_0, \quad (6)$$

the volume integral being taken through the same region as before.

Combining (5) and (6) we get

$$\begin{aligned} &\int \left( \frac{F \cos(nr_1)}{r_1^2} - \frac{G \cos(nr)}{r^2} \right) dS_0 \\ &= \int \left( \frac{F \cos(nr_1)}{r_1^2} - \frac{G \cos(nr)}{r^2} \right) dS \\ &\quad - \int \left( \frac{1}{r_1^2} \frac{dF}{dr_1} - \frac{1}{r^2} \frac{dG}{dr} \right) dv. \quad (7) \end{aligned}$$

If for  $S_0$  we choose a spherical surface of indefinitely small radius and centre at  $O$ , and if  $G_0$  is the value of  $G$  at  $O$ ,

this equation becomes

$$-4\pi G_0 = \int \left( \frac{F \cos(nr_1)}{r_1^2} - \frac{G \cos(nr)}{r^2} \right) dS, \quad (8)$$

provided that F and G are such that

$$\frac{1}{r_1^2} \frac{dF}{dr_1} - \frac{1}{r^2} \frac{dG}{dr} = 0;$$

that is, in virtue of (4),

$$\frac{1}{r_1^2} \frac{\partial F}{\partial r_1} - \frac{1}{r^2} \frac{\partial G}{\partial r} + \cos(r_1 r) \left( \frac{1}{r_1^2} \frac{\partial F}{\partial r} - \frac{1}{r^2} \frac{\partial G}{\partial r_1} \right) = 0.$$

Let us put

$$\frac{1}{r_1^2} \frac{\partial F}{\partial r_1} - \frac{1}{r^2} \frac{\partial G}{\partial r} = 0 \quad \dots \dots \dots (9)$$

and

$$\frac{1}{r_1^2} \frac{\partial F}{\partial r} - \frac{1}{r^2} \frac{\partial G}{\partial r_1} = 0. \quad \dots \dots \dots (10)$$

Then from (10) we shall have

$$\frac{F}{r_1^2} = \frac{\partial \phi}{\partial r_1}, \quad \frac{G}{r^2} = \frac{\partial \phi}{\partial r}, \quad \dots \dots \dots (11)$$

and using these values in (9) we get

$$\frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial \phi}{\partial r_1} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \phi}{\partial r} \right),$$

which may be written as

$$\frac{\partial^2}{\partial r_1^2} (r_1 r \phi) = \frac{\partial^2}{\partial r^2} (r_1 r \phi),$$

having for solution

$$r_1 r \phi = f(r_1 + r) + g(r_1 - r),$$

where  $f$  and  $g$  are any functions of  $r_1 + r$ , and  $r_1 - r$ .

If, therefore, we take  $\phi = \frac{1}{r_1 r} f \left( t - \frac{r_1 + r}{v} \right)$ , we get from (11) and (8)

$$\begin{aligned} & -4\pi \left[ r^2 \frac{\partial}{\partial r} \frac{1}{r_1 r} f \left( t - \frac{r_1 + r}{v} \right) \right]_{r=0} \\ & = \int \left[ \frac{\partial}{\partial r_1} \frac{1}{r_1 r} f \left( t - \frac{r_1 + r}{v} \right) \cos(nr_1) \right. \\ & \quad \left. - \frac{\partial}{\partial r} \frac{1}{r_1 r} f \left( t - \frac{r_1 + r}{v} \right) \cos(nr) \right] dS. \end{aligned}$$

The left-hand side of this equation is

$$\begin{aligned} -4\pi \left[ -\frac{1}{r_1} f\left(t - \frac{r_1 + r}{v}\right) - \frac{r}{r_1} f'\left(t - \frac{r_1 + r}{v}\right) \right]_{r=0} \\ = 4\pi \frac{1}{a} f\left(t - \frac{a}{v}\right) \\ = 4\pi s_0. \end{aligned}$$

Hence if we draw the normal inwards we have

$$\begin{aligned} 4\pi s_0 = \int \left[ \frac{\partial}{\partial r} \frac{\frac{1}{r_1} f\left(t - \frac{r_1 + r}{v}\right)}{r} \cos(nr) \right. \\ \left. - \frac{1}{r} \frac{\partial}{\partial r_1} \frac{1}{r_1} f\left(t - \frac{r_1 + r}{v}\right) \cos(nr_1) \right] dS \end{aligned}$$

as our required expression, or

$$\begin{aligned} 4\pi s_0 = \int \left[ \frac{\partial}{\partial r} \frac{s\left(t - \frac{r}{v}\right)}{r} \cos(nr) \right. \\ \left. - \frac{1}{r} \frac{\partial}{\partial r_1} s\left(t - \frac{r}{v}\right) \cos(nr_1) \right] dS \quad \dots \quad (12) \end{aligned}$$

If the normal is  $(l, m, n)$  and the origin is at O,

$$r_1^2 = (x+a)^2 + y^2 + z^2,$$

$$\begin{aligned} \text{and} \quad \frac{\partial s}{\partial r_1} \cos(nr_1) &= \frac{\partial s}{\partial r_1} \left( l \frac{x+a}{r_1} + m \frac{y}{r_1} + n \frac{z}{r_1} \right) \\ &= l \frac{\partial s}{\partial r_1} \frac{\partial r_1}{\partial x} + m \frac{\partial s}{\partial r_1} \frac{\partial r_1}{\partial y} + n \frac{\partial s}{\partial r_1} \frac{\partial r_1}{\partial z} \\ &= l \frac{\partial s}{\partial x} + m \frac{\partial s}{\partial y} + n \frac{\partial s}{\partial z} \\ &= \frac{\partial s}{\partial n}, \end{aligned}$$

and using this in (12) we get (1).

*XLIII. Theory of the Width of the Modified Spectrum Lines in the Compton Effect.* By G. E. M. JAUNCEY, D.Sc., Associate Professor of Physics, Washington University, St. Louis, U.S.A.\*

1. Introduction.

A. H. COMPTON† has proposed a theory of the scattering of X-rays based upon the postulate that each quantum of X-rays is scattered by an individual electron. This theory requires that the wave-length  $\lambda_\phi$  of the X-rays scattered in a direction  $\phi$  with the direction of the primary X-rays should differ from the wave-length  $\lambda_0$  of the primary rays by an amount

$$\lambda_\phi - \lambda_0 = h(1 - \cos \phi)/mc, \quad . \quad . \quad . \quad (1)$$

where  $h$  is Planck's constant,  $m$  is the rest mass of the electron, and  $c$  is the velocity of light. If the change of wave-length is expressed in Å.U., equation (1) may be written

$$\lambda_\phi - \lambda_0 = 0.0242(1 - \cos \phi). \quad . \quad . \quad . \quad (2)$$

Compton has tested this formula experimentally‡, and has found very good agreement with the theory when Mo K $\alpha$  X-rays are scattered by graphite. Compton's results for the scattering of Mo K $\alpha$  X-rays have been verified by others. However, all observers find that part of the X-rays are scattered with, and part without, change of wave-length. Compton calls the former modified scattered rays, and the latter unmodified rays. The unmodified rays give a spectrum line whose width is equal to that of the spectrum line of the primary rays. On the other hand, Compton's curves‡ show an increased width in the modified spectrum line. For instance, his curves for scattering at 90° show the modified spectrum line as having an extreme angular width of about 15 minutes of arc greater than the width of the unmodified line. This signifies a wave-length width of 0.027 Å.U. since a calcite crystal was used. Now the primary rays which are incident on the effective part of the scattering substance have an angular width of probably not more than 20°. This would account for a wave-length width of 0.008 Å.U. due to the variation of  $\phi$  in equation (2). There remains therefore a wave-length width of between 0.019 Å.U. and 0.027 Å.U. which is not due to the variation of  $\phi$ . In this paper it is sought to explain this width.

\* Communicated by the Author.

† A. H. Compton, Phys. Rev. xxi. p. 483 (1923).

‡ A. H. Compton, Phys. Rev. xxii. p. 408 (1923).

## 2. Theory.

The quantum theory of Compton \* is extended to the case where the binding energy of the electron has to be taken into account. The energy relation is then

$$hc/\lambda_0 = hc/\lambda_\phi + hc/\lambda_s + mc^2 \left( \frac{1}{\sqrt{1-\beta^2}} - 1 \right) + MV^2/2, \quad (3)$$

where  $\lambda_s$  is a critical absorption wave-length of the scattering substance, and where the third and fourth terms on the right-hand side represent the kinetic energy of the recoiling electron and that of the rest of the atom from which the recoil electron is separated respectively. This last term, however, is negligible, due to the mass of the rest of the atom being great compared with that of the recoil electron.

Next we consider the momentum relation. Referring to fig. 1, OA represents the magnitude and direction of the momentum of the primary quantum  $h/\lambda_0$ , OB the momentum of the scattered quantum  $h/\lambda_\phi$ , BC the momentum of the recoil electron  $m\beta c/\sqrt{1-\beta^2}$ , and CA the momentum of the rest of the atom from which the recoil electron is separated by the scattering process. We then have the vector equation

$$OA = OB + BC + CA, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where OA is along the  $x$ -axis and OB in the  $xy$  plane, but BC and CA are not necessarily in the  $xy$  plane. We next make the restriction that the momentum CA of the rest of the atom is equal but opposite in direction to the momentum of the electron in its Bohr orbit just before scattering takes place. The justification for this restriction is that the rest of the atom and the electron are each revolving about their common centre of mass before scattering takes place. If we assume that the action between the quantum and the electron takes place in a time very small compared with the period of the electron in its orbit, then the electron can be thought of as being suddenly removed from its orbit, and the centre of mass of the rest of the atom will continue in motion along the tangent to its orbit about the common centre of mass which existed just before the removal of the electron from the atom. Since the velocity due to thermal agitation is small, we may neglect the momentum of the atom as a whole before the removal of the electron. This requires that the momentum of the rest of the atom be equal and opposite to that of the electron before removal of the

\* A. H. Compton, Phys. Rev. xxi. p. 483 (1923).



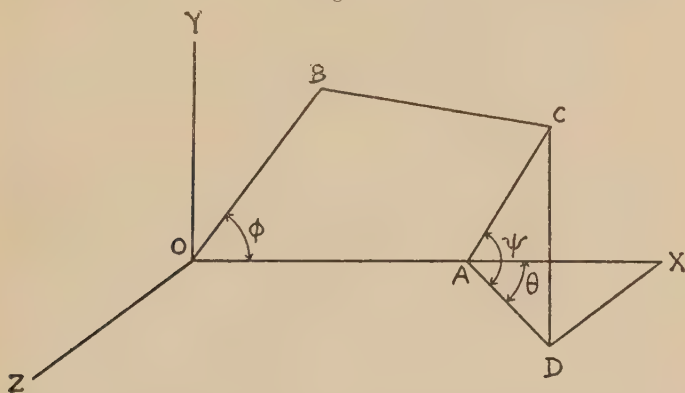
latter. We have therefore that AC ( $= -CA$ , fig. 1) represents the momentum of the electron in its Bohr orbit.

We shall now find an expression for the momentum of an electron in its Bohr orbit in terms of the binding energy of the electron in that orbit. For simplicity let us assume that the orbit is circular. Using the relativity mass of the electron at high speeds, we have the centrifugal force relation

$$\frac{m\beta_s^2 c^2}{r\sqrt{1-\beta_s^2}} = \frac{Ee}{r^2}, \quad . . . . . (5)$$

where  $r$  is the radius of the circular orbit,  $E$  is the effective nuclear charge, and  $\beta_s c$  is the velocity of the electron in its

Fig. 1.



orbit. The binding energy of the electron in its orbit is equal to minus the total energy of the electron in its orbit, and therefore

$$hc/\lambda_s = Ee/r + mc^2(1 - 1/\sqrt{1-\beta_s^2}). \quad . . . (6)$$

From equations (5) and (6) we obtain

$$\beta^2 = 2\alpha_s - \alpha_s^2, \quad . . . . . (7)$$

where  $\alpha_s = h/mc\lambda_s$ . The momentum of the electron in its orbit is therefore  $mca_n$ , where

$$\alpha_n = \beta_s/\sqrt{1-\beta_s^2} = \sqrt{2\alpha_s - \alpha_s^2}/(1-\alpha_s). \quad . . . (8)$$

The length of AC (fig. 1) represents  $mca_n$ , and is therefore constant. The locus of C is therefore a sphere with A as centre.

In fig. 1, AD is the projection of AC on the plane XOZ.

The angle CAD is represented by  $\psi$ , and the angle XAD by  $\theta$ . Since BC represents  $m\beta c/\sqrt{1-\beta^2}$ , we have, dividing throughout by  $m^2c^2$ ,

$$\begin{aligned}\beta^2/(1-\beta^2) &= \alpha_0^2 + \alpha_\phi^2 + \alpha_n^2 - 2\alpha_0\alpha_\phi \cos \phi \\ &\quad - 2\alpha_n\alpha_\phi \cos \psi \cos \theta \cos \phi \\ &\quad + 2\alpha_0\alpha_n \cos \psi \cos \theta - 2\alpha_\phi\alpha_n \sin \psi \sin \phi, \quad (9)\end{aligned}$$

where  $\alpha_0 = h/mc\lambda_0$  and  $\alpha_\phi = h/mc\lambda_\phi$ . From equation (3) we have, neglecting the energy of the rest of the atom,

$$\beta^2/(1-\beta^2) = \alpha_0^2 + \alpha_\phi^2 + \alpha_s^2 + 2\alpha_0 - 2\alpha_s - 2\alpha_0\alpha_\phi - 2\alpha_0\alpha_s + 2\alpha_\phi\alpha_s. \quad (10)$$

Equating the right-hand sides of equations (9) and (10), and solving for  $\alpha_\phi$ , we have

$$\alpha_\phi = \frac{\alpha_0(1 - \alpha_s - \alpha_n \cos \psi \cos \theta) - \alpha_s - (\alpha_n^2 - \alpha_s^2)/2}{1 + \alpha_0(1 - \cos \phi) - \alpha_s - \alpha_n(\cos \psi \cos \theta \cos \phi + \sin \psi \sin \phi)}. \quad (11)$$

Although equation (11) has been obtained on the assumption that the momentum of the rest of the atom is equal but opposite to that of the electron in its orbit, yet the equation is true even without this restriction provided that  $m\alpha_n$  is the momentum of the rest of the atom in the direction CA (fig. 1) after scattering has taken place. A. H. Compton\* has recently described a general quantum theory of scattering in which he arrives at an equation which is similar to equation (11). He however does not make the restriction given by equation (8), although he takes account of the binding energy of the electron in its orbit.

Referring to equation (11), we see that  $\alpha_\phi$  varies with  $\theta$  and  $\psi$ , the scattering angle  $\phi$  being constant. This variation of  $\alpha_\phi$  causes a variation of  $\lambda_\phi$ , the scattered wave-length due to the relation

$$\alpha_\phi = h/mc\lambda_\phi. \quad (12)$$

From equations (11) and (12) we have

$$\lambda_\phi = \lambda_0 \cdot \frac{w - v(\cos \psi \cos \theta \cos \phi + \sin \psi \sin \phi)}{u - v \cos \psi \cos \theta}, \quad (13)$$

where

$$u = 1 - \alpha_s - \alpha_s/\alpha_0 - (\alpha_n^2 - \alpha_s^2)/2\alpha_0,$$

$$v = \alpha_n,$$

and

$$w = 1 + \alpha_0(1 - \cos \phi) - \alpha_s.$$

\* A. H. Compton, Phys. Rev. xxiv, p. 168 (1924).

Let us move the origin of coordinates from O to A (fig. 1), and let the cartesian coordinates of C then be  $x, y, z$ , Since  $AC = \alpha_n = v = \text{constant}$ , we have  $\cos \psi \cos \theta = x/v$  and  $\sin \psi = y/v$ ; so that from equation (13)

$$\lambda_\phi = \lambda_0 \cdot \frac{w - x \cos \phi - y \sin \phi}{u - x} \quad . \quad . \quad . \quad (14)$$

Hence, for  $\lambda_\phi = \text{const.}$ , equation (14) shows that the locus of C is on the intersection of the plane represented by equation (14), and the sphere  $x^2 + y^2 + z^2 = v^2$ . Also, since there is no term in  $z$  in equation (14), the plane is parallel to the axis of  $z$ . The maximum and minimum values of  $\lambda_\phi$  ( $\phi = \text{const.}$ ) are therefore given by the two planes, equation (14), which touch the sphere. Since the planes are parallel to the axis of  $z$ , the problem reduces to finding the two lines in the  $xy$  plane which touch the circle  $x^2 + y^2 = v^2$ . Now the condition that the line represented by equation (14) may touch the circle is that

$$(u^2 - v^2)l^2 - 2(uw - v^2 \cos \phi)l + w^2 - u^2 = 0, \quad . \quad (15)$$

where  $l = \lambda_\phi / \lambda_0$ . Solving, we obtain

$$l = \frac{uw - v^2 \cos \phi \pm v \sqrt{u^2 + w^2 - 2uw \cos \phi - v^2 \sin^2 \phi}}{u^2 - v^2} \quad . \quad (16)$$

The extreme variation of  $\lambda_\phi$  is therefore

$$\delta \lambda_\phi = \frac{2v\lambda_0 \sqrt{u^2 + w^2 - 2uw \cos \phi - v^2 \sin^2 \phi}}{u^2 - v^2} \quad . \quad (17)$$

This is the formula for the wave-length width of a modified spectrum line in the Compton effect. The change of wave-length for the centre of the line is given by

$$\lambda_\phi - \lambda_0 = \lambda_0 \left( \frac{uw - v^2 \cos \phi}{u^2 - v^2} - 1 \right) \quad . \quad . \quad . \quad (18)$$

Equation (17), although exact, is difficult to handle. It may, however, be put into an approximate form which is sufficiently correct so long as  $\alpha$  is very much smaller than  $\alpha_0$ . We then have from equation (8) that  $\alpha_n = \sqrt{2\alpha_s}$ , and approximately  $u = 1$ ,  $v = \sqrt{2\alpha_s}$ , and  $w = 1$ . These approximations give

$$\delta \lambda_\phi = 4\lambda_0 \sin \frac{\phi}{2} \sqrt{2h/mc\lambda_s} \quad . \quad . \quad . \quad (19)$$

## 3. Comparison with Experiment, and Discussion.

For the scattering of Mo  $K\alpha$  X-rays by the  $L$  electrons of carbon we have  $\lambda_0 = 0.71 \text{ \AA.U.}$  and  $\lambda_s = 360 \text{ \AA.U.*}$ , making  $\alpha_0 = 0.034$  and  $\alpha_s = 0.000067$ . Inserting these values in equation (19), we have

$$\delta\lambda_\phi = 0.031 \sin \frac{\phi}{2} \dots \dots \dots (20)$$

For scattering at  $\phi = 90^\circ$ , equation (20) gives  $\delta\lambda_\phi = 0.022 \text{ \AA.U.}$ , while Compton's value, previously quoted, is less than  $0.027 \text{ \AA.U.}$  More recently Compton and Woo† have published experimental curves showing the change of wave-length of Mo  $K\alpha$  X-rays when scattered by various light elements. For scattering by carbon at  $\phi = 128^\circ$ , their curve shows  $\delta\lambda_\phi < 0.0264 \text{ \AA.U.}$ , while equation (20) gives  $\delta\lambda_\phi = 0.0278 \text{ \AA.U.}$  Thus for scattering by carbon, the experimental values agree fairly well with the theoretical values. Now, for scattering by the  $L$  electrons of aluminium,  $\lambda_s$  is about  $150 \text{ \AA.U.}$ , so that  $\alpha_s = 0.000162$ , and equation (19) becomes

$$\delta\lambda_\phi = 0.051 \sin \frac{\phi}{2} \dots \dots \dots (21)$$

Hence, scattering of Mo  $K\alpha$  X-rays by aluminium at  $\phi = 125^\circ$  should give  $\delta\lambda_\phi = 0.0454 \text{ \AA.U.}$  Compton and Woo's curve for aluminium shows about the same width for aluminium as for carbon—that is, less than  $0.027 \text{ \AA.U.}$  Hence it seems as though the theoretical formula predicts a width which is greater than the experimental value for aluminium.

Now equation (19) rests upon the restrictive assumption that the momentum of the rest of the atom is equal but opposite to that of the electron in its orbit just before scattering takes place, and this assumption rests upon the further assumption that the action between the quantum and the electron is sudden. However, "suddenness" is a relative term. The action probably has some duration of time. We can probably say that the action is sudden if its duration is small compared with the period of revolution of the electron in its Bohr orbit. As the atomic number increases, the period of revolution decreases. For a very slow action between the quantum and the electron the width would be very small, because in such a case the position of the electron in its orbit at the beginning of the action would have only a small effect on the change of wave-length. It would seem,

\* A. L. Hughes, Phil. Mag. xliii. p. 145 (1922).

† Compton and Woo, Proc. Nat. Acad. Sci. x. p. 271 (1924).

therefore, that my formula, equation (19), only holds for small values of  $\alpha_s$ ; that is, for small binding energies. For larger binding energies the experimental width is less than that given by equation (19)\*. A second reason for the smallness of the experimental width for aluminium is that in Compton and Woo's curve for aluminium the hump for the scattering by the L electrons includes also the scattering by the M electrons. The width of the line due to the M electrons is much smaller than that due to the L electrons. It should not be forgotten that we have only considered the electrons as revolving in circular orbits in our theory, whereas in a complete theory elliptic orbits should also be considered. The effect of elliptic orbits will be discussed in another article.

Just what would be the effect on the change of wave-length when the action between the quantum and the electron is slow depends upon what we assume to be the mechanical system of the inside of the atom, and very little is known is about intra-atomic mechanics. Compton †, in his paper on the general quantum theory of scattering, makes two alternative assumptions: (a) that  $\alpha_n = \alpha_s$ ,  $\theta = 0$ , and  $\psi = \pi$ ; and (b) that the momentum of the recoil electron is zero, although the electron is removed to the outside of the atom. Both of these assumptions require a slow action between the quantum and the electron. It appears to the writer that a careful study, both experimental and theoretical, of the width of the modified lines in the Compton effect for primary X-rays of various wave-lengths and for various scattering substances may throw some light on the time of the action between the quantum and the electron in the scattering process.

Washington University,  
St Louis, Mo., U.S.A.,  
July 24, 1924.

\* *Note added during proof reading.*—The restrictive assumption above mentioned is only valid if, in addition to the time of action being small, the time taken by the recoil electron in escaping from the electrostatic field of the rest of the atom after it has been removed from its Bohr orbit is small. Hence equations (17), (18), and (19) only hold for small values of the binding energy of the scattering electron. For values of the binding energy comparable with the energy of the primary quantum the wave-length width of the modified spectrum line is less than that given by equations (17) and (19).

† A. H. Compton, *Phys. Rev.* xxiv. p. 168 (1924).



XLIV. *A New Discussion of Bucherer's Experiment.*

By U. DOI\*.

[Plate VI.]

1. *Introductory Note.*

The present writer in 1922 † put forward a theory of relativity in which, however, Einsteinian relativity of space and time is excluded.

Following on a discussion with Einstein during his visit to Japan the writer has sought to obtain experimental evidence of his theory. Some investigations which support it will appear in the forthcoming 'Proceedings of the Physico-Mathematical Society of Japan.'

The following discussion of Bucherer's experiments, which is the main subject of the present paper, is taken up for the purpose of showing another example of experimental evidence therein in favour of the writer's theory, and against Einstein's one, contrary to what the author of the experiments, Bucherer, has concluded himself.

2. *Bucherer's Experiment.*

BY a very ingenious experiment, published in 1909 ‡, on the deflexion of the  $\beta$ -particles emitted with large velocities from radium fluoride set in the crossed field of electric and magnetic forces, Bucherer confirmed decisively that the amount of deflexion of an electron tends to zero as its velocity approaches that of light  $c$ . But the acceleration of an electron moving with the velocity  $v$  perpendicular to a magnetic field of the intensity  $H$  is proportional to  $\frac{e}{m} v H$ .

From an action of this sort in essence originated the above said deflexion of the  $\beta$ -particles in Bucherer's experiment. Thus, Bucherer's experimental conclusion as expressed by an equation is

$$\lim_{\beta=1} \frac{e}{m} \beta = 0,$$

in which  $\beta$  stands, as usual, for the ratio  $\frac{v}{c}$ . So far there may be no room for argument.

At the time when Bucherer experimentally confirmed the above relation there were prevailing two rival theories—one

\* Communicated by the Author.

† U. Doi, 'The Anti-Einstein Theory of Relativity,' 1922 (Japanese edition).

‡ *Ann. der Phys.* vol. xxviii. p. 513 (1909).

of Abraham and another of Lorentz—as to the constitution of an electron. So he made use of his experimental results, as his second step, to decide between these two rival theories. In this second step, Bucherer's conclusion from his data was that the preference was assuredly for the Lorentz theory, or, which comes to the same thing, for Einstein's theory of relativity.

On examining closer, however, the photographic records of the experiments, the present writer has found that they do not, either, afford evidence in favour of Lorentz-Einstein's theory. As will be seen in the following, on the contrary, there is exposed in them a serious discrepancy with what is claimed by that theory, while with the writer's theory they are in good agreement, almost to a degree of coincidence.

Now, fixing our attention to a particle with an initial velocity  $v$  in a direction making an angle  $\alpha$  with that of the magnetic field, the condition for it to escape from between the condenser plates is \*

$$evH \sin \alpha = eX, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $X$  is the electric intensity between the plates.

After leaving the plates, the particle follows a spiral path, deviating thus out of the vertical plane in which its initial motion has been confined. But it will be shown later in §4, that the amount of deviation of the sort is so small that the general form of the curve of velocity-function of an electromagnetic mass remains unaffected if we neglect it. And the matter is simplified. We have the above relation (1) for every  $\beta$ -particle that escapes from between the condenser plates, all the way along a circular arc confined within a respective vertical plane up to the photographic film. But the radius  $r$  of the circular arc described by the particle satisfies the equation

$$m \frac{v^2}{r} = evH \sin \alpha. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Elimination of  $v$  between the above two equations (1) and (2) gives

$$r = \frac{X}{H^2} \cdot \frac{m}{e} \cdot \frac{1}{\sin^2 \alpha} \cdot . \quad . \quad . \quad . \quad . \quad (3)$$

On the other hand we have

$$(r-z)^2 = r^2 - a^2, \\ \text{or} \quad z = r - \sqrt{r^2 - a^2}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where  $z$  is the amount of the vertical deflexion of the

\* For details the reader is referred to Bucherer's original paper.

particles on the film from the undeflected trace, and  $\alpha$ , the *effective* distance\* between the end of the condenser plates and the film. Thus, combining the equations (3) and (4), we are able to find the theoretically expected value of  $z$  corresponding to any assigned value for  $\alpha$ , provided the functional form of  $\frac{m}{e}$  in terms of  $\alpha$  is given.

Now, by Einstein's theory it is deduced to be, as is well known by the name of Lorentz's formula,

$$\frac{m}{e} = \frac{m_0}{\sqrt{1-\beta^2}} \cdot \frac{1}{e} = \frac{m_0}{e} \frac{1}{\sqrt{1-\beta^2}}.$$

But from the equation (1),

$$\beta = \frac{v}{c} = \frac{X}{cH} \frac{1}{\sin \alpha}.$$

Denoting  $\frac{X}{cH} = [\beta]_{\alpha=\frac{\pi}{2}}$  by  $\sin \alpha_0$  we have

$$\beta = \frac{\sin \alpha_0}{\sin \alpha}.$$

Thus,

$$\frac{m}{e} = \frac{m_0}{e} \frac{\sin \alpha}{\sqrt{\sin^2 \alpha - \sin^2 \alpha_0}}.$$

By the writer's theory, on the other hand, it is †

$$\frac{m}{e} = \frac{m_0}{(1-\beta^2)^2} \frac{e_0}{1-\beta^2} = \frac{m_0}{e_0} \frac{1}{1-\beta^2},$$

or

$$\frac{m}{e} = \frac{m_0}{e_0} \frac{\sin^2 \alpha}{\sin^2 \alpha - \sin^2 \alpha_0}.$$

Hence, according to Einstein's theory,

$$\left. \begin{aligned} z &= r - \sqrt{r^2 - a^2}, \\ r &= C_E \frac{1}{\sin \alpha \sqrt{\sin^2 \alpha - \sin^2 \alpha_0}}, \quad \left( C_E = \frac{X}{H^2} \frac{m_0}{e} \right); \end{aligned} \right\} \quad (5)$$

\* This *effective* distance is a little smaller than the actual geometrical one. Bucherer denotes it by  $a-p$ . See *Ann. der Phys.* loc. cit. p. 523.

† Author's 'Anti-Einstein Theory of Relativity,' loc. cit. p. 247.

while according to the other theory

$$\left. \begin{aligned} z &= r - \sqrt{r^2 - \alpha^2}, \\ r &= C_D \frac{1}{\sin^2 \alpha - \sin^2 \alpha_0}, \quad \left( C_D = \frac{X}{H^2} \frac{m_0}{e_0} \right). \end{aligned} \right\} \quad (6)$$

Comparing the calculated values for  $z$  with the actually obtained results on Bucherer's photographic films, we may be able to decide which of the two theories is to be preferred.

With Abraham's formula for  $\frac{m}{e}$ ,  $z$  is not so simple a function in terms of  $\alpha$  as in the above two equations. To avoid the complicated calculations for each separate photographic curve, therefore, Bucherer restricted himself to a comparison with one another of the maximum deflexions in a series of curves obtained with different conditions, which was sufficient, too, at the time for his purpose of distinguishing between Abraham's and Lorentz's formulæ.

In our present case, however, it is but an easy task to evaluate  $z$  corresponding to various values of  $\alpha$ , two or three, at most, significant figures being sufficient for our purpose. Indeed, the sets of equations (5) and (6) may be transformed, in form, respectively into

$$\left. \begin{aligned} z &= r - \sqrt{r^2 - \alpha^2} = r - r \cos \left( \sin^{-1} \frac{\alpha}{r} \right), \\ r &= C_E \frac{1}{\sin \alpha \sqrt{\sin^2 \alpha - \sin^2 \alpha_0}} = \frac{C_E}{\sin \alpha \{ \sin(\alpha + \alpha_0) \sin(\alpha - \alpha_0) \}^{\frac{1}{2}}}, \end{aligned} \right\} \quad (5)'$$

and

$$\left. \begin{aligned} z &= r - r \cos \left( \sin^{-1} \frac{\alpha}{r} \right), \\ r &= C_D \frac{1}{\sin^2 \alpha - \sin^2 \alpha_0} = \frac{C_D}{\sin(\alpha + \alpha_0) \sin(\alpha - \alpha_0)}. \end{aligned} \right\} \quad (6)'$$

The results of calculation are given in Table I. and Table II., corresponding respectively to Bucherer's experiments No. 7 and No. 15.

The figures in the last columns of both tables are rough results of the writer's readings, by means of a microscopic comparator, of the photographic curves on the negative plates reproduced in equal dimensions from the prints, in the *Annalen der Physik*, of Bucherer's original films. It will be seen at once that they are in by far the better agreement with the writer's values than with those of Lorentz-Einstein.

TABLE I.  
(For Experiment No. 7.)

$\alpha$ .	$\beta = \frac{v}{c}$ .	$x$ in mm.	$z_E$ in mm.	$z_D$ in mm.	$z_{\text{photogr.}}$ in mm.
25° 21' ...	0.9999	99	0	0	—
26° 21' ...	0.9645	97.47	0.69	0.20	—
27° 21' ...	0.9318	95.94	1.04	0.41	0.5
28° 21' ...	0.9015	94.41	1.30	0.62	0.7
29° 21' ...	0.8734	92.88	1.57	0.83	0.8
30° .....	0.8562	91.90	1.72	0.98	1.0
34° .....	0.7656	85.76	2.70	1.91	1.9
38° .....	0.6954	79.63	3.66	2.90	2.9
42° .....	0.6398	73.50	4.66	3.95	3.9
46° .....	0.5951	67.38	5.66	5.02	4.9
50° .....	0.5589	61.25	6.68	6.11	6.0
55° .....	0.5226	53.60	7.95	7.47	7.5
60° .....	0.4943	45.94	9.18	8.79	8.8
65° .....	0.4725	38.28	10.34	10.04	10.0
70° .....	0.4556	30.63	11.38	11.18	11.2
75° .....	0.4432	22.97	12.27	12.14	12.1
80° .....	0.4347	15.31	12.89	12.88	12.8
85° .....	0.4297	7.66	13.36	13.35	13.3
90° .....	0.4281	0	13.50	13.50	13.5

$$\log a = 0.59226, \quad \log C_E = 0.75805, \quad \log C_D = 0.71408.$$

$x$  measures the distance along the zero-line from the point of maximum deflexion, or the middle-point between the two vanishing ends of the curve.

### 3. Comparison of Theoretical with Photographic Curves.

It is not merely the matter of numerical values, however, that distinguishes the two theories from each other, but the essential character of the curve is different, as claimed by one or the other of the theories. There are two peculiar features, at least, worthy of our notice. First, the tangent of the angle of the limiting inclination of the curve at its vanishing ends to the undeflected line is infinite according to Einstein's equations (5), while it is finite according to the other (6). Next, according to (5), the curve is concave towards the undeflected line throughout the whole of its length; while, according to the other, it is convex at near its vanishing ends, and then becomes concave towards the undeflected line, thus giving a point of inflexion between the two regions of opposite concavity.



TABLE II.  
(For Experiment No. 15.)

$\alpha$ .	$\beta = \frac{v}{c}$ .	$x$ in mm.	$z_E$ in mm.	$z_D$ in mm.	$z_{\text{photogr.}}$ in mm.
31°.....	1.0007	95	0	0	—
32°.....	0.9727	93.39	0.75	0.21	—
33°.....	0.9464	91.78	1.08	0.41	0.5
34°.....	0.9217	90.17	1.39	0.62	0.7
35°.....	0.8986	88.56	1.65	0.84	0.9
37°.....	0.8565	85.34	2.12	1.27	1.2
40°.....	0.8019	80.51	2.80	1.96	2.0
42°.....	0.7703	77.29	3.24	2.41	2.5
45°.....	0.7289	72.46	3.90	3.11	3.2
47°.....	0.7048	69.24	4.34	3.58	3.6
50°.....	0.6728	64.41	4.98	4.28	4.3
52°.....	0.6541	61.19	5.41	4.75	4.7
55°.....	0.6292	56.36	6.03	5.45	5.4
57°.....	0.6146	53.14	6.43	5.89	5.9
60°.....	0.5952	48.30	7.03	6.56	6.5
65°.....	0.5687	40.25	7.94	7.60	—
70°.....	0.5485	32.20	8.75	8.52	8.5
75°.....	0.5336	24.16	9.43	9.28	9.3
80°.....	0.5234	16.10	9.93	9.87	9.9
85°.....	0.5174	8.05	10.25	10.23	10.2
90°.....	0.5154	0	10.35	10.35	10.3

$$\log a = 0.59226, \quad \log C_E = 0.83103, \quad \log C_D = 0.76410.$$

Differentiating, namely,  $z$  with respect to  $\alpha$  we have

$$\frac{dz}{d\alpha} = -\frac{dr}{d\alpha} \left( \frac{r}{\sqrt{r^2 - a^2}} - 1 \right),$$

$$\frac{d^2z}{d\alpha^2} = -\frac{d^2r}{d\alpha^2} \left( \frac{r}{\sqrt{r^2 - a^2}} - 1 \right) + \left( \frac{dr}{d\alpha} \right)^2 \frac{a^2}{(r^2 - a^2)^{3/2}}.$$

By Einstein's formula, then,

$$r = C_E \frac{1}{\sin \alpha \sqrt{\sin^2 \alpha - \sin^2 \alpha_0}},$$

$$\frac{dr}{d\alpha} = -C_E \cos \alpha \left\{ \frac{1}{\sin^2 \alpha \sqrt{\sin^2 \alpha - \sin^2 \alpha_0}} + \frac{1}{(\sin^2 \alpha - \sin^2 \alpha_0)^{3/2}} \right\},$$

and

$$\frac{d^2r}{d\alpha^2} = C_E \left\{ \frac{\sin^2 \alpha + 2 \cos^2 \alpha}{\sin^3 \alpha \sqrt{\sin^2 \alpha - \sin^2 \alpha_0}} + \frac{1}{\sin \alpha (\sin^2 \alpha - \sin^2 \alpha_0)^{3/2}} + \frac{3 \sin \alpha \cos^2 \alpha}{(\sin^2 \alpha - \sin^2 \alpha_0)^{5/2}} \right\}.$$

Hence, when  $\alpha$  is very near  $\alpha_0$ , or  $r$  very large,

$$\frac{dz}{d\alpha} = - \frac{dr}{d\alpha} \frac{a^2}{2r^2} = \frac{a^2}{2C_E} \cos \alpha \left\{ \sqrt{\sin^2 \alpha - \sin^2 \alpha_0} + \frac{\sin^2 \alpha}{\sqrt{\sin^2 \alpha - \sin^2 \alpha_0}} \right\}.$$

Thus, according to Einstein's formula we see, as above mentioned, that  $\frac{1}{R} \frac{dz}{d\alpha}$ , the tangent of the inclination of the curve traced by the  $\beta$ -particles against the undeflected line on the photographic film becomes positively infinite for  $\alpha = \alpha_0$  (provided, of course,  $\alpha_0 = \sin^{-1} \beta_0$  is not zero, and  $R$ , the radius of the film-circle, is finite, both of which were actually fulfilled in Bucherer's experiments,  $R$  having been equal to about 8 cm.).

By a similar step we have

$$\frac{1}{R^2} \frac{d^2z}{d\alpha^2} = - \frac{a^2}{2C_E R^2} \frac{\sin^3 \alpha \cos^2 \alpha}{(\sin^2 \alpha - \sin^2 \alpha_0)^{3/2}}.$$

The last expression is negatively infinite for  $\alpha = \alpha_0$ , showing that the curve is concave towards the undeflected line at its vanishing ends; and it remains as such up to the point of maximum deflexion.

With the writer's formula, on the other hand,

$$r = C_D \frac{1}{\sin^2 \alpha - \sin^2 \alpha_0},$$

$$\frac{dr}{d\alpha} = -C_D \frac{2 \sin \alpha \cos \alpha}{(\sin^2 \alpha - \sin^2 \alpha_0)^2},$$

and

$$\frac{d^2r}{d\alpha^2} = 2C_D \left\{ - \frac{\cos^2 \alpha - \sin^2 \alpha}{(\sin^2 \alpha - \sin^2 \alpha_0)^2} + \frac{4 \sin^2 \alpha \cos^2 \alpha}{(\sin^2 \alpha - \sin^2 \alpha_0)^3} \right\}.$$

Hence

$$\left[ \frac{dz}{d\alpha} \right]_{\alpha=\alpha_0} = \left[ \frac{a^2}{2C_D} \frac{2 \sin \alpha \cos \alpha}{(\sin^2 \alpha - \sin^2 \alpha_0)^2} \cdot (\sin^2 \alpha - \sin^2 \alpha_0)^2 \right]_{\alpha=\alpha_0} \\ = \frac{a^2}{2C_D} \sin 2\alpha_0 ;$$

or,  $\left[ \frac{dz}{R d\alpha} \right]_{\alpha=\alpha_0} = \frac{a^2}{2RC_D} \sin 2\alpha_0$ , which is approximately equal to 0.099 for Bucherer's experiment No. 15, while the photographic curve near its vanishing ends is seen to be elevated by about 1 mm. against 1 cm. of the zero-line.

Next,

$$\frac{d^2z}{d\alpha^2} = - \frac{d^2r}{d\alpha^2} \left( \frac{r}{\sqrt{r^2 - a^2}} - 1 \right) + \left( \frac{dr}{d\alpha} \right)^2 \frac{a^2}{(r^2 - a^2)^{3/2}},$$

which becomes approximately, as  $\alpha$  approaches  $\alpha_0$ , equal to

$$- \frac{a^2 d^2r}{2 d\alpha^2 r^2} + a^2 \left( \frac{dr}{d\alpha} \right)^2 \frac{1}{r^3} \\ = \frac{a^2}{C_D} (\cos^2 \alpha - \sin^2 \alpha).$$

Thus,

$$\left[ \frac{d^2z}{R^2 d\alpha^2} \right]_{\alpha=\alpha_0} = \frac{a^2}{R^2 C_D} \cos 2\alpha_0.$$

This last expression for  $\frac{d^2z}{R^2 d\alpha^2}$  is positive as long as  $\alpha_0$  lies between 0 and  $\frac{\pi}{4}$ , corresponding to the range of  $\sin \alpha_0$  from 0 up to 0.7071. But  $\sin \alpha_0$  corresponds, in its turn, to the velocity of the  $\beta$ -particles that undergo the maximum deflexion. In Bucherer's experiments it varied between 0.3173 and 0.6870, thus having been included within the above-mentioned range. According to the writer's theory, therefore, his photographic curves are all expected to be convex, contrary to what is claimed by Einstein's theory, near their vanishing ends towards the undeflected line. And at about  $\alpha = \frac{\pi}{4}$ \* there is expected a point of inflexion, where the curve turns its concavity to the opposite sense.

\* This is, of course, an approximate value,  $\left( \frac{a}{r} \right)^2$  and smaller quantities being neglected against unity. The magnitude of  $\left( \frac{a}{r} \right)^2$  for  $\alpha = \frac{\pi}{4}$  is, then, of the order :  
0.057 (Exper. No. 7),  
0.025 (Exper. No. 15).

As a matter of fact, then, a glancing inspection of Bucherer's photographic curves will be enough to appreciate that just apparently what is described above is actually exhibited in them.

To see the agreement and disagreement in a more contrasted manner, the theoretical data given in Tables I. and II. were plotted in five-fold magnification on a sheet of section paper. The theoretical curves obtained thus tracing through the plotted points were photographically reduced to their proper scale (Pl. VI. fig. 2). Then both the theoretical and Bucherer's experimental curves were at once fixed positively on the dry plates instead of on the developing paper. With these positive plates put together in pairs, and by means of an enlargement-apparatus, the negative plates were made for the theoretical curves superposed upon the experimental ones (Pl. VI. figs. 3 and 4).

#### 4. *Additional Remarks.*

In the above discussion every  $\beta$ -particle has been regarded as confined all over its path within a vertical plane determined by its initial direction of motion. Strictly speaking, however, the particle begins to deviate from that vertical plane under the action of the magnetic field at work, as soon as, after leaving the condenser plates, the vertical component of its velocity comes into existence. Only, the deviation of the sort did not amount in Bucherer's experiments to anything of such importance as to need being taken into consideration in the above discussion.

For the intensity of this disturbing action must be equal to  $ev \sin \phi H \cos \alpha$ , in which  $v \sin \phi$  stands for the vertical component of the velocity at the instant under consideration (see fig. 1). In the first approximation we may treat  $\alpha$  as a constant, and denoting by  $\xi$  the amount of deviation we have

$$m \frac{d^2 \xi}{dt^2} = ev \sin \phi H \cos \alpha.$$

But evidently  $v = r \frac{d\phi}{dt}$ , so that

$$m \frac{d^2 \xi}{dt^2} = er H \cos \alpha \cdot \sin \phi \frac{d\phi}{dt}.$$

Hence,

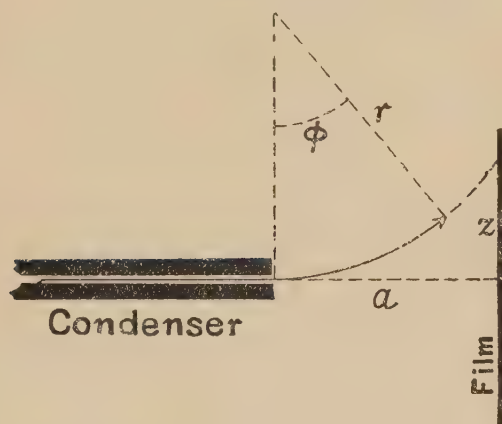
$$m \frac{d\xi}{dt} = -er H \cos \alpha \cdot \cos \phi + \text{const.}$$

The condition  $\frac{d\xi}{dt} = 0$  for  $\phi = 0$  determines the constant of integration in the last equation, and we have

$$m \frac{d\xi}{dt} = erH \cos \alpha (1 - \cos \phi) \\ = \frac{er^2 H \cos \alpha}{v} \left( \frac{d\phi}{dt} - \cos \phi \frac{d\phi}{dt} \right),$$

making use of  $v = r \frac{d\phi}{dt}$  once more.

Fig. 1.



Hence, further

$$m\xi = \frac{er^2 H \cos \alpha}{v} (\phi - \sin \phi) + \text{const.}$$

But  $\xi = 0$  for  $\phi = 0$ , so that finally

$$\xi = \frac{e}{m} \cdot \frac{r^2 H \cos \alpha}{v} (\phi - \sin \phi).$$

By a similar process the expression for  $z$  can be derived as

$$z = \frac{e}{m} \cdot \frac{r^2 H \sin \alpha}{v} (1 - \cos \phi)^*.$$

\* Putting  $\cos \phi = \frac{\sqrt{r^2 - a^2}}{r}$ , we have indeed

$$z = \frac{e}{m} \cdot \frac{r H \sin \alpha}{v} (r - \sqrt{r^2 - a^2}),$$

which is the combination of equations (2) and (4) p. 435 above.



Thus

$$\xi = z \cot \alpha \cdot \frac{\phi - \sin \phi}{1 - \cos \phi}.$$

For the particle arriving at the film,

$$\sin \phi = \frac{a}{r},$$

$$\cos \phi = \sqrt{1 - \left(\frac{a}{r}\right)^2} = 1 - \frac{1}{2}\left(\frac{a}{r}\right)^2 - \frac{1}{8}\left(\frac{a}{r}\right)^4 + \dots$$

$$\text{and } \phi = \sin^{-1} \frac{a}{r} = \frac{a}{r} + \frac{1}{2} \cdot \frac{1}{3} \left(\frac{a}{r}\right)^3 + \frac{3}{2 \cdot 4} \cdot \frac{1}{5} \left(\frac{a}{r}\right)^5 + \dots$$

Neglecting the small quantities of the order  $\left(\frac{a}{r}\right)^2$  against unity we have

$$\xi = \frac{1}{3} z \cdot \frac{a}{r} \cot \alpha.$$

Referring to the values for  $\xi$  given in Table III. (corresponding to Bucherer's experiment No. 15) and the actual appearance of the experimental curve (Pl. VI. fig. 1), it will be seen at once that the general character of the curve is still far from being affected by the deviation so far studied above. Indeed, the greatest value of  $\xi$  cannot possibly exceed 0.5 mm., while it is with difficulty that the point where the maximum deflexion is expected, or  $\alpha = \frac{\pi}{2}$ , is decided exactly to 1 mm. along the zero-line.

Before concluding the present discussion, one more remark should be added here, which bears some importance regarding the examination of Bucherer's experimental results.

He announces in the *Annalen der Physik* that the inner diameter of the cylinder was about 16 cm. round the inside of which the photographic films were extended. The expected distance along the film, therefore, between the two vanishing ends of the photographic curve is :

$$\begin{aligned} l &= 2 \times 8 \text{ cm. } \left( \frac{\pi}{2} - \alpha_0 \right) \\ &= 16 \left( \frac{\pi}{2} - \sin^{-1} \beta_0 \right) \text{ cm.} \end{aligned}$$

Thus,

$$l = 18 \text{ cm., for Exper. No. 7 ;}$$

and

$$l = 16.5 \text{ cm., for Exper. No. 15.}$$

TABLE III.—(For Experiment No. 15.)

$\alpha$ .	$\log \cot \alpha$ .	$\log \frac{a}{r}$ .	$\log z$ .	$\xi = \frac{1}{3} z \frac{a}{r} \cot \alpha$ .
31°.....	0.22123	2.01989	$\infty$	0 mm.
35°.....	0.15477	2.63246	1.92428	0.02
40°.....	0.07619	2.99815	0.29226	0.08
45°.....	0.00000	1.19873	0.49276	0.16
47°.....	1.96966	1.25889	0.55388	0.20
50°.....	1.92381	1.33541	0.63144	0.26
52°.....	1.89281	1.37923	0.67669	0.30
55°.....	1.84523	1.43640	0.73640	0.35
57°.....	1.81252	1.46973	0.77012	0.38
60°.....	1.76144	1.51365	0.81690	0.41
62°.....	1.72567	1.53939	0.84386	0.43
65°.....	1.66867	1.57332	0.88081	0.44
67°.....	1.62785	1.59312	0.90200	0.44
70°.....	1.56107	1.61897	0.93044	0.43
75°.....	1.42805	1.65276	0.96755	0.37
80°.....	1.24632	1.67608	0.99432	0.28
85°.....	1.94195	1.68977	1.00988	0.15
90°.....	$\infty$	1.69429	1.01494	0

Rough estimation of the lengths of Bucherer's photographic curves will show at once that these expected values are far too low. With 8 cm. for the inner radius of the cylinder and the actual lengths of the photographic curves

$$l = 19.8 \text{ cm. (about), for Exper. No. 7,}$$

$$\text{and } l = 19.0 \text{ cm. (about), for Exper. No. 15,}$$

we shall have respectively

$$\frac{\pi}{2} - \alpha'_0 = 70^\circ.9 \text{ instead of } \frac{\pi}{2} - \alpha_0 = 64^\circ.65 \text{ (No. 7),}$$

$$\text{and } \frac{\pi}{2} - \alpha'_0 = 68^\circ.0 \text{ instead of } \frac{\pi}{2} - \alpha_0 = 58^\circ.97 \text{ (No. 15);}$$

and consequently

$$\beta'_0 = 0.327 \text{ instead of Bucherer's } \beta_0 = 0.4281 \text{ (No. 7),}$$

$$\text{and } \beta'_0 = 0.374 \text{ instead of Bucherer's } \beta_0 = 0.5154 \text{ (No. 15).}$$

Now, it may be too far here to enter into any speculative inquiry as to what disturbing cause should have given rise to the above-mentioned discrepancies. And yet it may be noticed, all the same, that some systematic or other error must have anyhow been inherent to Bucherer's estimation of the effective field-intensities at work. Whether the terminal voltage applied to the condenser plates may have suffered a drop due to the current, if it were ever so feeble, flowing between the plates, cannot be said positively.

At any rate, it is preferable, it may dare be said however, not to evaluate the absolute value of  $\frac{e}{m}$  for small velocities from Bucherer's experimental data, and the writer is inclined to stop at, and not to go any further from, regarding the very high merit of the experiments as lying in an elegant photographic representation of the general character of the velocity-function for  $\frac{e}{m}$ . It is sufficient for us by itself alone to distinguish decisively between the different theories of the constitution of the electron.

For the absolute value of  $\frac{e}{m}$  for small velocities, then, we had better turn with Sommerfeld \* to another region of our experimental knowledge. From the universally accepted constant of electrolysis we have,

$$\frac{e}{m_H} = 2.872 \times 10^{14} \text{ e.s.u.};$$

and the recently obtained spectroscopic data of the hydrogen and helium Balmer series enable us with the help of Bohr's theory to estimate

$$\frac{m_H}{m} = 1847.$$

Thus the value of  $\frac{e}{m}$  for small velocities is determined, to a sufficient degree of accuracy, to be

$$\frac{e_0}{m_0} = 5.305 \times 10^{17} \text{ e.s.u.},$$

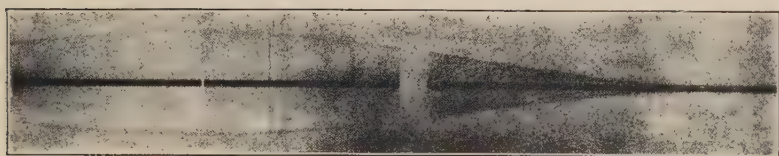
and

$$= 1.769 \times 10^7 \text{ e.m.u.},$$

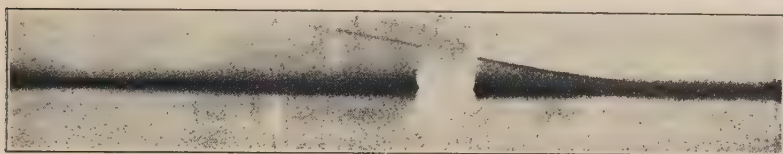
the value that is most reliable at present.

Physical Institute, Faculty of Science,  
Imperial University of Tokyo, Japan,  
June 1924.

\* A. Sommerfeld, *Atombau und Spektrallinien*, 3rd edition, p. 272.

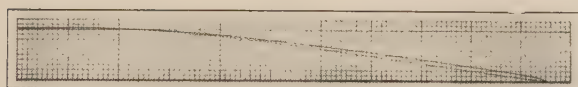


(No. 1.)

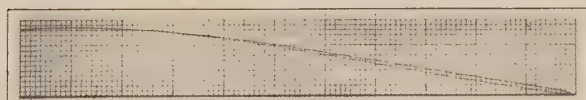


(No. 7.)

A. H. Bucherer.

FIG. 1. (Taken from the *Annalen der Physik*, IV. vol. xxviii., 1909).

(No. 15.)



(No. 7.)

FIG. 2.

Full line ——— for Einstein's curve; dotted line ... for Doi's curve.



FIG. 3. (For Experiment No. 15).

The middle point between the two vanishing ends lies at about 3 mm. to the left of the original mark on the zero-line.



FIG. 4 (For Experiment No. 7).

Not the centre-line, but the upper margin, of the broad undeflected trace is to be regarded as the zero-line with Bucherer's value  $z_{\text{max.}} = 13.5$  mm.





XLV. *On the Stabilization of Instable Equilibrium by means of Gyroscopic Forces.* By Dr. H. J. E. BETH (Deventer)\*.

**T**HOMSON and TAIT have † investigated the equilibrium of a dynamical system when, besides forces deriving from a force function, gyroscopic forces are working on the system. An important part of the results they arrived at may be expressed in this manner:—If the number of the instabilities which the system possesses (taking away the gyroscopic forces) is an odd number, it is impossible to stabilize the equilibrium by the means of gyroscopic forces. Moreover, several examples are treated of instable equilibrium with an even number of instabilities where stabilization by the means of such forces appeared to be possible. The general observation was made that the gyroscopic forces will dominate if they become of sufficient greatness.

In this paper I will prove that stabilization of instable equilibrium with an even number of instabilities by means of gyroscopic forces is *always* possible, and I will derive the conditions which must be fulfilled by those forces ‡.

We start from the determinantal equation

$$D \equiv \begin{vmatrix} m^2 + a_{11} & a_{12}m & a_{13}m & \dots & a_{1n}m \\ -a_{12}m & m^2 + a_{22} & a_{23}m & \dots & a_{2n}m \\ -a_{13}m & -a_{23}m & m^2 + a_{33} & \dots & a_{3n}m \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -a_{1n}m & -a_{2n}m & -a_{3n}m & \dots & m^2 + a_{nn} \end{vmatrix} = 0 \quad (1)$$

for a mechanism having  $n$  degrees of freedom.

The coefficients  $a_{11}, a_{22}, \dots, a_{nn}$  arise from the potential energy, the coefficients  $a_{12}, a_{13},$  etc. from the gyroscopic forces. If all gyroscopic coefficients are zero, the equation (1) passes into

$$(m^2 + a_{11})(m^2 + a_{22}) \dots (m^2 + a_{nn}) = 0.$$

Now we suppose the equilibrium without gyroscopic forces to be instable; therefore not all coefficients  $a_{11}, a_{22}, \dots, a_{nn}$  are positive. We may suppose an even number  $l$  of them to be negative.

\* Communicated by the Author.

† 'A Treatise of Natural Philosophy,' i. p. 391, etc.

‡ The question was set by the Mathematical Society of Amsterdam for the year 1923.

Therefore in the equation

$$D \equiv \begin{vmatrix} m_2 + a_{11} & a_{12}m & \dots & a_{1l}m & \dots & a_{1n}m \\ -a_{12}m & m^2 + a_{22} & \dots & a_{2l}m & \dots & a_{2n}m \\ -a_{13}m & -a_{23}m & \dots & a_{3l}m & \dots & a_{3n}m \\ \vdots & \vdots & & \vdots & & \vdots \\ -a_{1l}m & -a_{2l}m & \dots & m^2 + a_{ll} & \dots & a_{ln}m \\ -a_{1,l+1}m & -a_{2,l+1}m & \dots & \dots & \dots & a_{l+1,n}m \\ \vdots & \vdots & & \vdots & & \vdots \\ -a_{1n}m & -a_{2n}m & \dots & \dots & \dots & m^2 + a_{nn} \end{vmatrix} = 0$$

the coefficients  $a_{11}, a_{22}, \dots, a_{ll}$  are negative,  $a_{l+1,l+1}, \dots, a_{nn}$  are positive. We will prove that it is possible to choose the values of the coefficients  $a_{12}, a_{13}, \dots$  in such a way that the equation  $D=0$  has its roots negative.

We take for this purpose

$$\begin{aligned} a_{1,l+1} &= 0, & a_{2,l+1} &= 0, \dots, a_{l+1,l+1} &= 0, \\ a_{1,l+2} &= 0, & a_{2,l+2} &= 0, & a_{l+2,n} &= 0, \\ & \vdots & & & & \\ a_{1n} &= 0, & a_{2n} &= 0, & a_{nn} &= 0, \end{aligned}$$

by which the equation passes into

$$D \equiv \begin{vmatrix} m^2 + a_{11} & a_{12}m & \dots & a_{1l}m \\ -a_{12}m & m^2 + a_{22} & \dots & a_{2l}m \\ \dots & \vdots & & \vdots \\ (m^2 + a_{l+1,l+1}) & \vdots & & \vdots \\ \dots & -a_{1l}m & \dots & m^2 + a_{ll} \end{vmatrix} = 0.$$

Of the equation  $D=0$ ,  $n-l$  roots  $m^2$  are equal to  $-a_{l+1,l+1}, -a_{l+2,l+2}, \dots, -a_{nn}$ , which roots are negative; from this it follows that the  $n-l$  stabilities are maintained.

The system of  $n$  degrees of freedom with partial stability has now been reduced to a system of  $l$  degrees of freedom, possessing only instabilities. Its determinantal equation

$$\Delta \equiv \begin{vmatrix} m^2 + a_{11} & a_{12}m & \dots & a_{1l}m \\ -a_{12}m & m^2 + a_{22} & \dots & a_{2l}m \\ \vdots & \vdots & & \vdots \\ -a_{1l}m & -a_{2l}m & \dots & m^2 + a_{ll} \end{vmatrix} = 0. \quad (2)$$

contains the  $l$  remaining roots  $m^2$ . We have to prove still that the coefficients  $a_{12}, a_{13}, \dots$  may be chosen in such a way that the equation  $\Delta=0$  has its roots negative;  $a_{11}, a_{22}, \dots, a_{ll}$  are all negative.

We put

$$m = \frac{m'}{\lambda}, \quad a_{12} = \frac{c_{12}}{\lambda} \dots \dots a_{l-1,l} = \frac{c_{l-1,l}}{\lambda},$$

$\lambda$  being a parameter. The equation passes into

$$\begin{vmatrix} m'^2 + a_{11}\lambda^2 & c_{12}m' & \dots & c_{1l}m' \\ -c_{12}m' & m'^2 + a_{22}\lambda^2 & \dots & c_{2l}m' \\ \vdots & \vdots & \ddots & \vdots \\ -c_{1l}m' & -c_{2l}m' & \dots & m'^2 + a_{ll}\lambda^2 \end{vmatrix} = 0. \quad (3)$$

Now we suppose

$$|a_{ik}| \neq 0 \quad (a_{ik} = -a_{ki}, \quad a_{kk} = 0), \quad . \quad . \quad . \quad (4)$$

and therefore

$$|c_{ik}| \neq 0 \quad (c_{ik} = -c_{ki}, \quad c_{kk} = 0). \quad . \quad . \quad . \quad (4a)$$

When  $\lambda$  approaches zero the roots may be divided into two classes: those of the second class approach to a finite limit different from zero; those of the first class approach zero, and the ratios of one of the roots and  $\lambda^4$  is different from zero.

The roots  $m'^2$  of the second class are given by

$$d \equiv \begin{vmatrix} m' & c_{12} & \dots & c_{1l} \\ -c_{12} & m' & \dots & c_{2l} \\ \dots & \dots & \ddots & \dots \\ -c_{1l} & -c_{2l} & \dots & m' \end{vmatrix} = 0. \quad . \quad . \quad (5)$$

In order to obtain the remaining roots  $m^2$ , we substitute in (3)  $m' = \frac{\lambda^2}{m''}$ ; the equation passes into

$$\begin{vmatrix} \lambda^2 + a_{11}m''^{1/2} & c_{12}m'' & \dots & c_{1l}m'' \\ -c_{12}m'' & \lambda^2 + a_{22}m''^{1/2} & \dots & c_{2l}m'' \\ \dots & \dots & \ddots & \dots \\ -c_{1l}m'' & -c_{2l}m'' & \dots & \lambda^2 + a_{ll}m''^{1/2} \end{vmatrix} = 0,$$

which equation has  $\frac{1}{2}l$  roots  $m''^{1/2}$  of moderate value, and  $\frac{1}{2}l$  roots

of order  $\lambda^4$ . The roots of the first class are approximately given by

$$\left. \begin{array}{cccc} a_{11}m'' & c_{12} & \dots & c_{1l} \\ -c_{12} & a_{22}m'' & \dots & c_{2l} \\ \dots & \dots & \dots & \dots \\ -c_{1l} & -c_{2l} & \dots & a_{ll}m'' \end{array} \right\} = 0. \quad (6)$$

The roots  $m''$  of this equation have the sign of those roots  $m''$  of (3), which are not given by (5). We therefore have to prove that the roots  $m''$  of (5) and the roots  $m''$  of (6) are all negative if the coefficients  $a_{12}, a_{13}, \dots$  have been chosen well.

In the first place we prove that the roots  $m''$  of (5) are negative provided the condition (4a) is fulfilled. For this purpose we start from (3) with the supposition that  $a_n, a_{22}, \dots, a_{ll}$  are all positive. It is a well-known fact that in this case all roots of  $m^3$  of (2) are negative\* (it is the analytical expression of the fact that stable equilibrium may never be lost by gyroscopic forces). The proposition holds good for small values of  $\lambda$ . If  $\lambda=0$ ,  $\frac{1}{2}l$  roots  $m''$  become zero, and the other remain negative; these roots, however, are given by (5).

In the second place we prove that with the same condition the roots  $m''$  of (6) are negative. If we substitute

$$a_{11} = -a_{11}', \quad a_{22} = -a_{22}', \quad \dots, \quad a_{ll} = -a_{ll}',$$

we may also write (6)

$$\left. \begin{array}{cccc} a_{11}'m'' & c_{12} & \dots & c_{1l} \\ -c_{12} & a_{22}'m'' & \dots & c_{2l} \\ \dots & \dots & \dots & \dots \\ -c_{1l} & -c_{2l} & \dots & a_{ll}'m'' \end{array} \right\} = 0.$$

When we divide the elements of the first row and those of the first column by  $\sqrt{a_{11}'}$ , those of the second row and of the second column by  $\sqrt{a_{22}'}$ , and so on, then a determinantal equation arises in the shape of (5) with other values of the  $c$ ; however, the new  $c$  fulfil the condition (4a); so the roots  $m''$  of (6) are negative.

Therefore stabilization may always be obtained by values of  $a_{12}, a_{13}, \dots$ , which are of sufficient greatness and which fulfil the inequality (4).

\* A proof is to be found in Routh, 'Stability of Motion,' p. 77.

XLVI. *On the Impact with Liquid Surfaces of Solid Bodies of Various Shapes.* By G. ERIC BELL, B.Sc., *Physics Research Laboratory, University College, Nottingham* \*.

[Plate VII.]

**I**N a previous paper† the author discussed in some detail the phenomena attending the impact of solid spheres with fluid surfaces, and showed that they were dependent on

- (1) The surface tension of the liquid ;
- (2) The viscosity of the liquid ;
- (3) The condition of the surface of the body.

As was previously observed by Worthington‡, this last factor is by far the most important. In the present paper an account is given of research on the impact of solid bodies with liquids, with particular reference to the shape of the bodies.

The research was carried out with exactly the same apparatus as the previous work, and in exactly the same manner. Shadow photographs were obtained showing the state of the body and liquid at various short intervals of time after the impact, a typical selection of which is reproduced in Pl. VII.

In all these photographs the height of fall is such that the velocity of the body on entering the liquid is of the order 250 cm. per sec.

In the first series of photographs, Pl. VII. fig. 1 (*a, b, & c*), a cylinder of length 4.4 cm. and diameter 0.8 cm. was allowed to fall into water, the surface of the cylinder being first carefully cleaned and polished. The same cylinder was then again cleaned and polished, and coated thinly with a layer of paraffin oil, giving the results shown in fig. 2 (*a, b, & c*). Throughout all these experiments, the photographs obtained with a surface coated with paraffin oil may be regarded as typical of the general effects of coating the body with a layer of a substance of low surface-tension. Many such substances were tried, such as various oils, turpentine, and alcohol, and the photographs only differ in minute details not considered for the present purpose.

In the series shown in figs. 3 (*a, b, & c*) and 4 (*a, b, & c*)

\* Communicated by Prof. E. H. Barton, D.Sc., F.R.S.

† Phil. Mag. xlviii. p. 753 (November 1924).

‡ Phil. Trans. Roy. Soc. A, cxci. (1897) and A, ccxxv. (1900).



the process was repeated, using a cylinder 3.15 cm. long and 0.56 cm. diameter. The similarity between the photographs for the large cylinder and the small one is very striking. (Fig. 1 is to be compared with fig. 3, and fig. 2 with fig. 4.) This is true throughout all the photographs taken.

One end of each cylinder was then turned hemispherical, and the resulting body polished, and another two series of photographs taken. Typical examples are shown in figs. 5 (*a, b, & c*) and 6 (*a, b, & c*), the surface being clean in the first case, soiled in the second.

The other end of each cylinder was then turned hemispherical, giving a body hemispherical at each end, and other photographs taken, giving the results shown in figs. 7 (*a, b, & c*) and 8 (*a, b, & c*).

Finally, the impact of a body pointed at one end and hemispherical at the other was studied, the result being shown in figs. 9 (*a, b, & c*) and 10 (*a, b, & c*).

The three photographs of fig. 11 may be considered as typical of the phenomena occurring when a body is allowed to fall into a liquid of low surface-tension—in this particular case turpentine.

#### *Analysis of the Photographs.*

It will be seen from the reproductions in Pl. VII. that when a perfectly clean cylinder is allowed to fall into water, there is a considerable disturbance in the liquid, and a large air-cavity of considerable size and curious shape is produced. The most noteworthy point about this air-cavity is that it closes up very rapidly at the mouth. The actual disturbance at the surface itself is very slight; if, however, the same cylinder is coated with paraffin oil, a considerable surface-disturbance occurs, and the tendency of the air-cavity to close in at the surface disappears: the cavity continues to get wider right to the surface. It will further be noticed that the basin-like surface-disturbance is completely formed almost as soon as the end of the cylinder penetrates the liquid-surface.

Turning to the case when the end of the cylinder is made hemispherical and the surface clean, we observe that the body penetrates the surface with no disturbance—a phenomenon observed by Worthington (*loc. cit.*) for a sphere falling slowly. There is this difference, however, that while a sphere under conditions of comparatively low impact-velocity makes no air-cavity, the cylinder draws

after it a long, nearly cylindrical cavity. The difference in shape between this cavity and that produced by a sphere (described in the previous paper) is very remarkable. This particular type of splash seems to be the counterpart for an elongated body with a hemispherical nose and flat top of the "smooth" splash caused by spherical bodies.

Again, if the surface is coated with paraffin oil (or other oil), a pronounced surface-disturbance makes its appearance, and the air-cavity forms a neck.

A body which is round at both ends, and clean, penetrates the surface without disturbance, and the liquid closes over the top without drawing after it an air-cavity. We have, in fact, a "smooth" splash. When this body is coated with paraffin oil, it makes a disturbance of exactly the same kind as that caused by a body rounded at one end only.

A body which is pointed at one end produces a "smooth" splash, whether its surface is clean or coated with an oil-film. The body used in this case is not so highly polished as in the previous cases, and a small air-bubble adheres to its upper surface, which shows ripple-marks.

#### *Explanation of the Results.*

These observations may be summarized as follows :—

- (1) A pronounced surface-disturbance never appears when the bodies used are clean and free from surface-films, and the liquid into which they fall has a high surface-tension, provided that the height of fall is not too great.
- (2) The surface-disturbance, if any, is produced by the nose immediately after penetration.
- (3) The pointed body used does not produce an air-cavity and surface-disturbance, even if its surface is coated with an oil-film, for these impact-velocities.
- (4) An air-cavity is produced by a blunt nose. This cavity remains open if the surface of the body is contaminated, but rapidly closes if the surface is clean.
- (5) An air-cavity is drawn down if the upper end of the body is flat; this cavity remains nearly cylindrical if the body is clean, but assumes a different form if the body is coated with an oil-film.

These various phenomena receive an explanation, at least qualitatively, by considering the forces acting on an

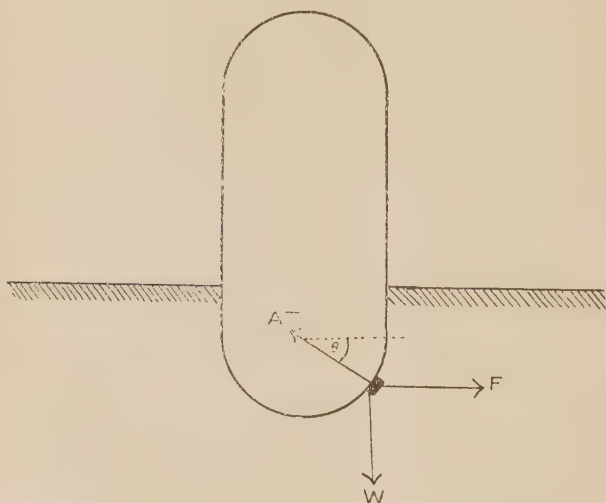
element of the fluid in contact with the impinging body. We may consider three such forces :—

- (1) A force  $F$ , tending to cause the liquid to flow horizontally outwards with a certain velocity. This force may be considered as constant for any given body, whatever the state of its surface; it is a function of the velocity only.
- (2) The force due to surface-tension round the boundary of the liquid in contact with the body. The result is a force, say  $AT$ , normally inwards,  $A$  being a constant.
- (3) A force  $P$ , normally inwards, due to hydrostatic pressure. As we shall only consider the effects immediately after impact, and near the surface, this may be neglected.
- (4) The weight of the liquid acting vertically downwards, of magnitude, say,  $W$ .

#### *The Surface Disturbance.*

Consider the forces acting on a small prism of the liquid, one face of which is in contact with the body.

Fig. 1.



The various forces act as shown in fig. 1. Consider the special case of a body with a hemispherical end, and take

spherical coordinates, of which the origin is the centre of the hemisphere. Let the coordinates of the portion of liquid considered be  $(r, \theta, 0)$ .

Then the horizontal force tending to draw the liquid away from the solid surface is given by

$$F - AT \cos \theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the vertical force urging the liquid upwards is

$$AT \sin \theta - W. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The equations cannot be expected to hold for  $\theta = \frac{\pi}{2}$ , because the forces will not have had time to be established, and also because the area of cross-section of the body immersed in the liquid will be very small.

From equation (1) we see that the force tending to draw the liquid away from the body is greater if the surface-tension is reduced. Hence, if a liquid of low surface-tension is used, or if the body is coated with a layer of a liquid of low surface-tension, the cavity should form more easily—which the photographs show to be the case. Further, an increase in the height of fall, which increases  $F$ , tends to cause an open air-cavity to form. It is also apparent from equation (1) that the cavity, if formed at all, will be formed very soon after impact, when  $\cos \theta$  is small, which again is known to be the case.

Further, if the body fall in such a manner that a cavity is formed, it is evident that the liquid has both a horizontal and vertical velocity, which, on account of internal friction etc., will be less for portions of the liquid near to the body than for portions further away. This vertical velocity, which tends to increase the surface of the liquid, will diminish more rapidly if the surface-tension and viscosity of the liquid are greater. Thus, for liquids like water and turpentine, which have viscosities of the same order but very different surface-tensions, the upshot rim should be greater in the case of turpentine, the surface of the body being the same in each case. This is the case, as is shown in figs. 5 and 11 of Pl. VII. of this paper. With increase of viscosity, both the height of the upshot rim and the width of the cavity will be less, as is shown to be the case in the photographs of the previous paper, where glycerine of high viscosity is used as the main liquid.

It further appears from equations (1) and (2) that for high entrance-velocities the horizontal component of the velocity of the liquid will be increased and the vertical component slightly diminished. Thus the upshot rim should be more open at the top for high falls than for low falls. This is experimentally shown to be true in the photographs obtained by Worthington (*loc. cit.*).

Similar considerations hold for the upper end of the body. If it is rounded, there is a resultant force tending to hold the liquid to the surface of the body, and hence cause a "smooth" splash. On the other hand, if the upper surface is flat the liquid leaves the surface, and an air-cavity is produced as shown in fig. 5 of Pl. VII.

The case of the pointed body affords another verification of these principles.

The expression giving the resultant force tending to draw the liquid away from the body,  $F - AT \cos \theta$ , shows that, if  $AT \cos \theta < F$ , the liquid clings to the body and no cavity is formed. Now, for a pointed body  $\theta$  is always of a definite value, and if the point is sharp,  $\cos \theta$  is large. Thus the liquid does not easily flow away; figs. 9 and 10 of the plate show that, for the particular body used,  $AT \cos \theta$  remains greater than  $F$ , even when  $T$  is reduced by coating the surface with paraffin oil.

It can be experimentally shown that if the height of fall is increased (thus increasing  $F$ ), or if the point is made more blunt (thus decreasing  $\cos \theta$ ), a rough splash may be produced.

### *Summary.*

In this paper the splashes caused by bodies of various shapes falling into liquids are discussed. It is shown that the type of splash depends jointly on the shape of the nose of the body and on the state of its surface. A simple scheme is outlined which explains these results qualitatively.

<sup>\*</sup> University College, Nottingham,  
November 28, 1924.



FIG. 1.



FIG. 2.



FIG. 3.



FIG. 4.

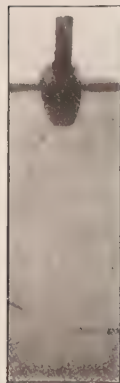


FIG. 5.

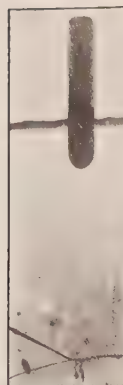


FIG. 6.



FIG. 7.

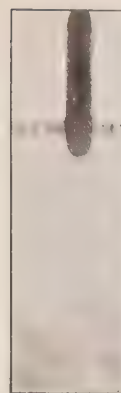


FIG. 8.

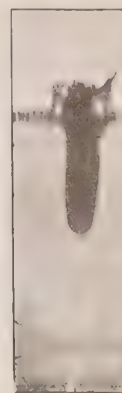


FIG. 9.

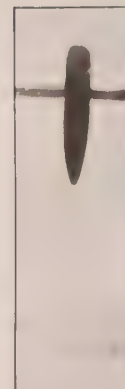


FIG. 10.



FIG. 11.



a

a

b

b

c

c

Shape.....

Cylinder (Large).

Cylinder (Large).

Cylinder (Small).

Cylinder (Small).

Cylinder round at one end.

Cylinder round at one end.

Cylinder round at both ends.

Cylinder round at both ends.

Pointed at one end, round at other.

Pointed at one end, round at other.

Cylinder round at one end, falling into turpentine.

State of Surface }

Clean.

Coated with oil.

Clean.

Coated with oil.

Clean.

Coated with oil.

Clean.

Coated with oil.

Clean.

Coated with oil.

Clean.



XLVII. *On Eddington's Natural Unit of the Field, and Possible Relations between it and the Universal Constants of Physics.* By J. RICE, M.A., Associate-Professor in the Department of Physics, University of Liverpool\*.

IN a paper published three years ago in the 'Proceedings of the Royal Society'† and more recently in his book on Relativity‡, Professor Eddington has put forward a very attractive hypothesis which he calls the Principle of Identification. He points out that two avenues of scientific investigation initially widely separated have gradually converged: one, the *deductive* study of pure geometry; the other, the *inductive* study of "the physical world consisting of space, time, and things." On the one hand, the geometers have developed a pure geometry, making use of certain tensors which possess definite properties *by virtue of mathematical identities*; on the other hand, the physicists have been led, owing to the rise of the Relativity Principle, to introduce into mathematical physics tensors possessing definite properties *by reason of those generalizations from experiment which we refer to as the laws of conservation of energy and momentum, the laws of the electromagnetic field, and the law of gravitation.*

It appears that in several cases the properties possessed by a geometrical tensor are identical with those possessed by one of the physical tensors. This suggests that if any further advance be made in physical science, conforming presumably to the Principle of Relativity and therefore involving the introduction of fresh tensors in its mathematical formulation, it may be possible to discover geometrical tensors possessing by virtue of identities just the same properties as the newly-introduced physical tensors possess by reason of experimental fact. If we can in general apply with success this "Principle of Identification," we can hardly go further in physical theory. (It is, as Eddington remarks, a problem for the psychologist rather than for the physicist to determine how the mind is cognisant of those physical quantities whose behaviour is so closely simulated by a world of entities constructed out of that relation-structure which is described in pure geometry.) Such an application finds but little favour in certain quarters, where it is described as a "geometrization of physics." It would appear, however, to be

\* Communicated by the Author.

† Proc. Roy. Soc. A, xcix. pp. 104-123 (May 1921).

‡ 'The Mathematical Theory of Relativity' (Camb. Univ. Press 1923).

just as reasonable to assert that the method is "physicising geometry." In any case, nothing more serious seems to be in question than the apparently innocuous result that the mathematical material most suited to the treatment of the properties of a four-dimensional manifold turns out to be also the most convenient implement for expressing the general principles to which physicists have been led by their own experimental observations.

One interesting suggestion arising out of this Principle of Identification concerns natural units in which physical quantities may be measured. Supposing we accept the hypothesis put forward by Einstein and de Sitter that space is finite though unbounded; and suppose we also adopt Eddington's view that Einstein's law of gravitation

$$G_{\mu\nu} = \lambda g_{\mu\nu}$$

in an empty region is really a gauging equation which gives to the world all the most important properties of a world of uniform curvature, not because of any innate tendency in the world to this symmetrical form, but because we adapt our natural gauge of length at different points and in different directions to make it so. Then it would seem that the radius of curvature of this world should be the natural unit of length on which the units employed in the geometrical tensors should be based. But if there be an underlying connexion between geometrical and physical tensors, such a fundamental unit of length might conceivably lead to the discovery of natural units in which to measure physical quantities. In fact, in the paper referred to, Eddington has attempted to arrive at a natural unit in which to express the matter-tensor  $T_{\mu\nu}$ , and the electromagnetic energy-tensor  $E_{\mu\nu}$ . When expressed in such a unit, it would be reasonable to assume that  $T_{\mu\nu} = E_{\mu\nu}$  in an electromagnetic field, while in space containing electrons  $T_{\mu\nu} - E_{\mu\nu}$  would represent a tensor corresponding to the non-Maxwellian stresses which preserve the electron from disintegration under the mutual repulsion of its parts. The reasoning in this part of the paper referred to is based on a Hamiltonian variation of the invariant integral

$$\int *G_{\alpha\beta} *G^{\beta\alpha} \sqrt{(-g)} d\tau,$$

where  $*G_{\mu\nu}$  is contracted from the curvature in-tensor  $*R^\kappa_{\lambda\mu\nu}$ , and  $d\tau$  is the element of four-dimensional space.

In what follows, the writer attempts to arrive at Eddington's conclusions in a different and possibly more direct manner.

The in-tensor  $*G_{\mu\nu}$  resolves itself naturally into two parts, a symmetric tensor  $R_{\mu\nu}$  and an anti-symmetric tensor  $F_{\mu\nu}$ . Now consider a system of coordinates in which the unit-mesh has a width  $\lambda^{-\frac{1}{2}}$  cm., where  $\lambda$  cm.<sup>-2</sup> is the world curvature. This means that observers considering the local part of the world as referred to a Galilean system of coordinates will regard two points on the  $x_\mu$  axis at a distance apart of 1 cm. as having a  $\delta x_\mu$  equal to  $\lambda^{\frac{1}{2}}$ . Let us also use the length  $\lambda^{-\frac{1}{2}}$  cm. as a gauge. Such a gauge-coordinate system could plausibly be taken as fundamental in so far as determination of the units of physical magnitude is concerned; not, of course, in any sense in which it could be considered as privileged, for that would violate the Relativity Principle.

Now in such a gauge-coordinate system the metric tensor  $g_{\mu\nu}$  is simply given by

$$R_{\mu\nu} = g_{\mu\nu}.$$

From  $g_{\mu\nu}$  we construct, as usual, the Christoffel indices  $\{\lambda\mu, \nu\}$ , and thence the Riemannian curvature tensor  $R_{\lambda\mu\nu}^\kappa$  and the Einstein tensor  $G_{\mu\nu}$ . We can write

$$R_{\mu\nu} = G_{\mu\nu} + H_{\mu\nu},$$

where  $H_{\mu\nu}$  is a symmetric tensor, which Eddington surmises is connected in some way not yet explained with the non-Maxwellian binding stresses on the electron. But we have no further concern with  $H_{\mu\nu}$  here.

In this coordinate-gauge system the matter-tensor is identified with

$$G_\mu^\nu - \frac{1}{2}g_\mu^\nu (G - 2). \quad . \quad . \quad . \quad . \quad (1)$$

The electromagnetic energy-tensor is identified with

$$F_{\mu\alpha}F^{\nu\alpha} - \frac{1}{4}g_\mu^\nu F_{\alpha\beta}F^{\alpha\beta}. \quad . \quad . \quad . \quad . \quad (2)$$

A certain similarity in their construction appears if we write (1) in the form

$$R_{\mu\alpha}G^{\nu\alpha} - \frac{1}{2}g_\mu^\nu (R_{\alpha\beta}G^{\alpha\beta} - 2),$$

which is true since  $R_{\mu\nu} = g_{\mu\nu}$ . Making the plausible assumption that the physical tensors which have been so identified with the geometrical tensors (1) and (2) are in this gauge system expressed in the same unit, we can then say that in an electromagnetic field

$$G_\mu^\nu - \frac{1}{2}g_\mu^\nu (G - 2) = F_{\mu\alpha}F^{\nu\alpha} - \frac{1}{4}g_\mu^\nu F_{\alpha\beta}F^{\alpha\beta}. \quad . \quad . \quad (3)$$



Let us now transform to a system in which the gauge is one centimetre, and in which a local Galilean frame will make the coordinate difference for two points one centimetre apart on an axis equal to unity. If accented symbols are used for this system, we have

$$R_{\alpha\beta}\delta x_\alpha\delta x_\beta = R'_{\alpha\beta}\delta x'_\alpha\delta x'_\beta,$$

for  $R_{\mu\nu}$  is an in-tensor, and so  $R_{\alpha\beta}\delta x_\alpha\delta x_\beta$  is an invariant.

As  $\delta x'_\mu = \lambda^{-\frac{1}{2}}\delta x_\mu$ , it follows that

$$R'_{\mu\nu} = \lambda R_{\mu\nu}.$$

But in this gauge-coordinate system we know that

$$R'_{\mu\nu} = \lambda g'_{\mu\nu}.$$

Hence

$$g'_{\mu\nu} = g_{\mu\nu}.$$

Since  $\lambda$  is a constant, it appears on considering the manner by which the  $G'_{\mu\nu}$  are constructed from the  $g'_{\mu\nu}$  and their differential-coefficients that

$$G'_{\mu\nu} = \lambda G_{\mu\nu}.$$

As  $F_{\mu\nu}$  is an in-tensor, it follows, as in the case of  $R_{\mu\nu}$ , that

$$F'_{\mu\nu} = \lambda F_{\mu\nu}$$

and therefore

$$H'_{\mu\nu} = \lambda H_{\mu\nu}.$$

It is also true (since  $g'_{\mu\nu} = g_{\mu\nu}$ ) that

$$G'^{\mu\nu} = \lambda G^{\mu\nu},$$

$$G'_{\mu}{}^{\nu} = \lambda G_{\mu}{}^{\nu},$$

and

$$G' = \lambda G.$$

Hence, by (3),

$$F'_{\lambda\alpha}F'^{\mu\alpha} - \frac{1}{4}g'^{\mu\nu}F'_{\alpha\beta}F'^{\alpha\beta} = \lambda^{-1}[G'_{\mu}{}^{\nu} - \frac{1}{2}g'^{\mu\nu}(G' - 2\lambda)].$$

The left-hand side of this equation is  $-E_{\mu}{}^{\nu}$  where  $E_{\mu}{}^{\nu}$  is the electromagnetic energy-tensor, the field-components being expressed in Eddington's natural field-unit. By the law of gravitation

$$G'_{\mu}{}^{\nu} - \frac{1}{2}g'^{\mu\nu}(G' - 2\lambda) = -8\pi\kappa T'^{\mu}{}_{\nu},$$

where  $T'^{\mu}{}_{\nu}$  is the matter-tensor expressed in c.g.s. units (*i. e.*, units in which the mass-density arising from the

component  $T'^{44}$  of the contravariant tensor is in grams per c.c.), and  $\kappa$  is the quotient of the astronomical constant by the square of the velocity of light (approximately  $7.4 \times 10^{-29}$  in c.g.s. units).

Hence

$$E_{\mu}^{\nu} = 8\pi\kappa\lambda^{-1}T'_{\mu}{}^{\nu},$$

and in particular

$$E_4^4 = 8\pi\kappa\lambda^{-1}T'^4_4, \quad . \quad . \quad . \quad . \quad (4)$$

where  $E_4^4 = \frac{1}{2}(e^2 + h^2)$ ,  $e$  and  $h$  being the values of the electric and magnetic intensities of the field *in natural units*.

Consider an electrostatic field whose intensity is 1 natural-unit, so that  $e=1$ ,  $h=0$ ; let its value be  $b$  electrostatic units; the energy-density of this field is  $b^2/8\pi$  ergs per c.c., and therefore

$$T'^4_4 = b^2/8\pi c^2,$$

where  $c$  is the velocity of light. Hence by (4)

$$\frac{1}{2} = 8\pi\kappa\lambda^{-1}b^2/8\pi c^2;$$

$$\text{i. e., } b = c\sqrt{(\lambda/2\kappa)},$$

or the natural unit of field is

$$c\sqrt{(\lambda/2\kappa)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in electrostatic units.

In the paper quoted, Eddington assumes  $\lambda$  to be of the order  $10^{-50}$ , taking the radius of curvature of the world to be of the order  $10^7$  parsecs ( $3 \times 10^{25}$  cm.). This makes the natural field-unit of the same order as the electrostatic unit of field. Lately, however, opinion seems to be tending to a much smaller value for the curvature. Thus de Sitter and Shapley estimate values for the radius of curvature approaching  $10^{10}$  parsecs, while in a recent communication to 'Nature' (March 8 and April 26, 1924) Silberstein suggests a value as high as  $5 \times 10^{12}$  parsecs. If we take Silberstein's value, making  $\lambda$  of the order  $10^{-62}$ , it gives us less than a millionth of an electrostatic unit as the order of magnitude of Eddington's natural field-unit.

From this unit field it is easy to obtain natural units for other physical quantities, and it is interesting to speculate on a possible connexion between such units and the universal constants of physical science. Thus, if we denote the radius of curvature of the world by  $R$ , we can introduce a "cosmic" unit of electric charge (to use Weyl's term). Representing this unit by  $\epsilon$  ordinary units (electrostatic), we define it by

$$\begin{aligned} \epsilon/R^2 &= \text{unit field} \\ &= c\sqrt{(\lambda/2\kappa)}. \end{aligned}$$

Using de Sitter's cosmology in which  $\lambda = 3/R^2$ , we get

$$2\kappa\epsilon^2/3c^2R = R.$$

Now, taking the mass of the electron as  $2e^2/3c^2r$ , where  $r$  is the electrical radius of the electron, we have

$$2\kappa\epsilon^2/3c^2r = \rho,$$

where  $\rho$  is the gravitational radius of the electron ; so that

$$\epsilon^2/e^2 = R^2/r\rho. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This shows that the "cosmic" unit of action  $\epsilon^2/c$  (approximately the same as that calculated by Eddington in the references given above) and what we might call the "electronic" unit of action  $e^2/c$  are connected by the relative dimensions of the world and the electron. This suggests that the cosmic unit and the Planck quantum of action,  $h$ , may be connected in a similar fashion. The discovery of some fundamental connexion between the electronic unit of action and the quantum number is one of the problems of physical theory, and several interesting guesses at the nature of the pure number  $hc/e^2$  have been offered. It may not be out of place to suggest that the cosmic unit and the Planck quantum may be related to one another through the size of the world and the size of some simple structure which enters into the make-up of "things." It seems obvious to propose the electron for the latter, but the numerical result obtained thereby is quite hopeless unless a value of the order  $10^7$  parsecs is chosen for  $R$ , which appears improbable. It occurs to the writer that since the quantum underlies in some mysterious way the dynamics of atomic phenomena, it may be plausible to assume that the structure referred to ought to contain an atomic dimension ; *e. g.*, the distance apart of nucleus and electron in the simplest combination of these two elements, *viz.*, the normal hydrogen atom. Thus taking this structure as a "tube" stretching from nucleus to electron, and writing  $a$  for the radius of the first Bohr circular orbit of the hydrogen atom, let us postulate that the cosmic unit of action and the Planck quantum have the same ratio as the volume of the world and the volume of this structure ; *i. e.*,

$$\epsilon^2/hc = \pi^2 R^3/\pi a r^2,$$

and so by (6)

$$e^2/hc = \pi R \rho / a r.$$

Now if  $m$  be the mass of the electron, we know by Bohr's

theory that

$$a = h^2 / 4\pi^2 m e^2 ;$$

therefore

$$\begin{aligned} e^2 / hc &= 4\pi^3 R \rho m e^2 / h^2 r \\ &= (8\pi^3 / 3) (e^2 / hc)^2 \cdot R \rho / r^2. \end{aligned}$$

Hence

$$R \rho = (3hc / 8\pi^3 e^2) r^2. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Relation (7) would fit in very well with the suggestion familiar to relativists (see Eddington's 'Space, Time, and Gravitation,' p. 179) that the electrical radius of the electron is of the same order of magnitude as the mean proportional between its gravitational radius and the radius of the world. It also gives a value of the order  $10^{12}$  parsecs for  $R$  ( $2 \times 10^{12}$ , however, instead of Silberstein's  $5 \times 10^{12}$ ). Were it possible to write  $8\pi^3/3$  for  $hc/e^2$ , the relation (7) would take quite an elegant form :

$$R \rho = \pi^2 r^2.$$

Unfortunately the well-determined values for  $h$  and  $e$  seem to rule this out. At one time it appeared possible that  $\pi^6$  might be equated to  $hc/e^2$ ; but although  $8\pi^5/3$  (approx. 816) is a better approximation than  $\pi^6$  to the value of  $hc/e^2$  (approx. 861, if  $e = 4.78 \times 10^{-10}$ ;  $h = 6.55 \times 10^{-27}$ ), it seems equally impossible. The preceding considerations, however, suggest that in some unknown way the important pure number  $hc/e^2$  may be contained in the metrical relations of the structure of the world.

It may be of interest to point out that the energy-density of the unit field, *i. e.*,  $\lambda/16\pi\kappa$  in *mass* units, is one-quarter of the density of the "world matter" required to fill the world on Einstein's own cosmology. Briefly, twice the natural field, if omnipresent, would on Einstein's views "swell out" the world to its proper size.

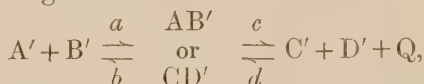
#### XLVIII. *The Critical Increment of Chemical Reactions.*

By WILLIAM EDWARD GARNER \*.

**I**N the usual interpretation of the physical meaning of the constant  $A$  in the Arrhenius equation  $d \log k / dT = A/RT^2$ , it has been assumed that the experimental velocity constant  $k_1$  corresponds to the velocity constant of the activations process. Thus, for a bimolecular reaction it is assumed that every collision between active molecules, or between

\* Communicated by the Author.

molecules whose kinetic energies exceed a critical value, leads to chemical change. This conclusion would appear to be unsound, for there is no reason why a collision between active molecules should not give rise to reactants as well as to the resultants of the chemical reaction. If we assume the momentary formation of complexes between the reacting molecules, then the bimolecular reaction can be expressed by the following scheme :



where reaction is assumed to occur between the activated molecules  $A'$  and  $B'$  and  $C'$  and  $D'$  respectively, to give the complex  $AB'$  or  $CD'$ , which can then dissociate to give either the substances on the left or the right hand of the equation. There will be four distinct reactions,  $a$ ,  $b$ ,  $c$ , and  $d$ , and the corresponding velocity constants  $k_a$ ,  $k_b$ ,  $k_c$ , and  $k_d$ \*. If  $k_1$  is the measured velocity constant for the reaction  $A + B \longrightarrow C + D$ , it is clear that  $k_1 = k_a \cdot k_c / (k_c + k_b)$ , where  $k_c / (k_c + k_b)$  is the fraction of the number of complexes which break down to give  $C$  and  $D$ .

Now the number of gram. mols. of complex formed from  $A$  and  $B$  per second  $= k_a[A][B]$ , and the number of molecules  $= k_a N[A][B]$  where  $N$  is the Avogadro number, and if  $m$  and  $n$  represent the numbers of active molecules of  $A$  and  $B$  per gram. mol. and  $k$  is the number of collisions per litre per second between two molecules, then

$$k_a N[A][B] = kmn[A][B];$$

$$\therefore k_1 = kmnk_c / N(k_c + k_b);$$

and since  $k$  varies very slightly with temperature,

$$d \log mn / dT = -A/RT^2 - d \log (k_c / (k_c + k_b)) / dT.$$

The equilibrium between active and inactive molecules must be established very rapidly if the laws of mass action are to hold. Thus, in the equilibrium between  $A'$  molecules and  $A$  molecules, we shall have

$$d \log (m/N) / dT = -q_A / RT^2,$$

where  $q_A$  is the energy of activation for the change,  $A \rightleftharpoons A'$ ; similarly

$$d \log (n/N) / dT = -q_B / RT^2.$$

\*  $k_a$  is the velocity constant for the reaction  $A + B \longrightarrow AB'$ , and  $k_d$  for the reaction  $C + D \longrightarrow CD'$ , expressed in gm. mols. per sec.



Thus

$$d \log mn/dT = -(q_A + q_B)/RT^2,$$

whence

$$(q_A + q_B)/RT^2 = A/RT^2 + d \log (k_c/k_c + k_b)/dT.$$

Thus  $q_A + q_B = \Sigma h\nu$  the activation energy of the reactants may be greater or less than  $A$  the Arrhenius constant, according as the temperature coefficient of  $k_c/k_c + k_b$  is negative or positive. The average energy of the complexes will increase with temperature; thus there is no *a priori* reason why  $k_c/k_c + k_b$  should be independent of temperature. It follows that the critical increment is not necessarily the same as the activations energy, and that  $\nu$  calculated therefrom may not coincide with the actual absorption bands of the reactants.

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University College, London.  
Dec. 7th, 1924.

XLIX. *Tides in a Channel.* By J. PROUDMAN (*Tidal Institute, University of Liverpool*) \*.

1. **T**HE present investigation † relates to the tidal dynamics of a channel whose section is uniform along the length but of varying depth from side to side.

A short conjectural treatment of the problem was given by Sir G. B. Airy ('Tides and Waves,' §§ 358-363), but one of his results, viz. that "the ridge of wave cannot possibly stretch transversely to the channel," is erroneous, as will be seen below (§ 2). Another of his results, viz. a rule for the direction of rotation of tidal currents, is valid, however, over wider conditions than Airy considered (§ 3).

After making general deductions concerning a section of any shape, attention is concentrated on a parabolic section (§ 4). One result is to show the degree of accuracy involved in the approximations of what may be called the "narrow sea theory." This is the theory which in recent years has been shown, notably by R. Sterneck and A. Defant, to account for many of the observed features of tides in gulfs, channels, and narrow seas.

\* Communicated by the Author.

† Part of the Adams Prize Essay, 1923. The author is much indebted to Dr. A. T. Doodson for the calculations involved in the illustrations.

The essential characteristic of the narrow sea theory is that transverse currents are neglected, so that the motion is assumed to consist of longitudinal oscillations whose currents maintain oscillating transverse gradients in virtue of the Earth's rotation. By introducing geometrical simplicity into the basin it is possible to take account of the transverse currents and then to compare the results with those obtained on neglecting these currents. We find that if the channel is not too wide or too shallow the degree of accuracy of the narrow sea theory is high, but that this degree of accuracy decreases as the effect of the Earth's rotation becomes important.

## 2. General Equations.

We shall denote by

- $\omega$  the component of the Earth's angular velocity along the vertical at the latitude of the channel,
- $g$  the acceleration due to gravity,
- $x, y$  Cartesian coordinates of position in the longitudinal and transverse directions respectively,
- $a_1, a_2$  the values of  $y$  along the sides of the channel, so that the breadth of the channel is  $a_2 - a_1$ ,
- $h$  the depth of water below any point of the mean surface,
- $A$  the area of a vertical transverse section of the channel,
- $t$  the time,
- $\zeta$  the elevation of the free surface of the water at any time above any point on the mean surface,
- $\bar{\zeta}$  the mean elevation at any time along the surface-line of any transverse section,
- $u, v$  the longitudinal and transverse components of current at any point and time,
- $\bar{u}$  the mean value of the longitudinal component of current over any vertical transverse section at any time.

We shall suppose that the motion is "small" and retain only terms of the first order.

The equation of continuity takes the form

$$\frac{\partial}{\partial x}(hu) + \frac{\partial}{\partial y}(hv) + \frac{\partial \zeta}{\partial t} = 0, \quad . \quad . \quad . \quad (2.11)$$

while at the sides of the channel we have

$$hv \rightarrow 0, \quad \text{as} \quad y \rightarrow a_1, a_2. \quad . \quad . \quad . \quad (2.12)$$

In the absence of astronomical and frictional forces the equations of motion take the form

$$\frac{\partial u}{\partial t} - 2\omega v = -g \frac{\partial \xi}{\partial x}, \quad \frac{\partial v}{\partial t} + 2\omega u = -g \frac{\partial \xi}{\partial y}. \quad (2.13)$$

Now suppose that

$$\left. \begin{aligned} \xi &= Z \cos(\sigma t - \kappa x), \\ u &= U \cos(\sigma t - \kappa x), \\ v &= V \sin(\sigma t - \kappa x), \end{aligned} \right\} \quad . \quad . \quad . \quad (2.21)$$

where  $\sigma$  and  $\kappa$  are constants, and  $Z$ ,  $U$ ,  $V$  are functions only of  $y$ . We regard  $\sigma$  as prescribed so that the values of  $\kappa$  will be determined by the basin. On substituting from (2.21) into (2.11) and (2.13), we obtain

$$\kappa h U + \frac{d}{dy}(hV) - \sigma Z = 0, \quad . \quad . \quad . \quad (2.22)$$

$$\sigma U + 2\omega V = \kappa g Z, \quad \sigma V + 2\omega U = -g \frac{dZ}{dy}, \quad (2.23)$$

and then deduce

$$\frac{d}{dy}(hV) - \frac{2\omega}{\sigma} \kappa h V = \frac{\kappa^2}{\sigma} \left( \frac{\sigma^2}{\kappa^2} - gh \right) Z. \quad . \quad (2.24)$$

From (2.24) and the boundary condition at  $y=a_1$  we deduce

$$hV = \frac{\kappa^2}{\sigma} e^{\frac{2\omega}{\sigma} \kappa y} \int_{a_1}^y \left( \frac{\sigma^2}{\kappa^2} - gh \right) Z e^{-\frac{2\omega}{\sigma} \kappa y} dy, \quad . \quad (2.25)$$

so that the boundary condition at  $y=a_2$  gives

$$\int_{a_1}^{a_2} \left( \frac{\sigma^2}{\kappa^2} - gh \right) Z e^{-\frac{2\omega}{\sigma} \kappa y} dy = 0. \quad . \quad . \quad (2.26)$$

On solving equations (2.23) we have, providing  $\sigma \neq \pm 2\omega$ ,

$$\frac{\sigma^2 - 4\omega^2}{\sigma g} U = \kappa Z + \frac{2\omega}{\sigma} \frac{dZ}{dy}, \quad \frac{\sigma^2 - 4\omega^2}{\sigma g} V = -\frac{dZ}{dy} - \frac{2\omega}{\sigma} \kappa Z, \quad . \quad . \quad . \quad (2.27)$$

and then on substituting into (2.22) we have

$$\frac{d}{dy} \left( h \frac{dZ}{dy} \right) + \left( \frac{\sigma^2 - 4\omega^2}{g} - \kappa^2 h + \frac{2\omega}{\sigma} \kappa \frac{dh}{dy} \right) Z = 0. \quad (2.28)$$

The condition to be satisfied at the sides may be written as

$$h \left( \frac{dZ}{dy} + \frac{2\omega}{\sigma} \kappa Z \right) \rightarrow 0, \quad y \rightarrow a_1, a_2. \quad . \quad . \quad (2.29)$$

The special cases  $\sigma = \pm 2\omega$  require separate treatment. We take  $\sigma = 2\omega$ , which corresponds to a semi-diurnal tide at the North Pole or to a diurnal tide in north latitude  $30^\circ$ .

The equations (2.23) take the form

$$\frac{\sigma}{g}(U + V) = \kappa Z = -\frac{dZ}{dy}, \quad . \quad . \quad . \quad (2.31)$$

so that

$$\kappa Z = e^{-\kappa y}, \quad . \quad . \quad . \quad . \quad . \quad (2.32)$$

on dropping a constant numerical factor. Equation (2.26) then becomes

$$\int_{a_1}^{a_2} \left( \frac{\sigma^2}{\kappa^2} - gh \right) e^{-2\kappa y} dy = 0, \quad . \quad . \quad . \quad (2.33)$$

and we notice that there is only one real value of  $\kappa$ .

In the "narrow sea theory" equation (2.11) is replaced by

$$\frac{\partial}{\partial x}(A\bar{u}) + (a_2 - a_1) \frac{\partial \bar{\xi}}{\partial t} = 0, \quad . \quad . \quad . \quad (2.41)$$

while equations (2.13) are replaced by

$$\frac{\partial \bar{u}}{\partial t} = -g \frac{\partial \bar{\xi}}{\partial x}, \quad 2\omega \bar{u} = -g \frac{\partial \bar{\xi}}{\partial y}, \quad . \quad . \quad (2.42)$$

though of course in applications  $A$  and  $a_2 - a_1$  are functions of  $x$ . Then (2.22) becomes replaced by

$$\kappa \bar{U} - \sigma / \bar{h} \cdot \bar{Z} = 0, \quad . \quad . \quad . \quad . \quad (2.43)$$

where

$$\bar{h} = A / (a_2 - a_1) = \int_{a_1}^{a_2} h dy / \int_{a_1}^{a_2} dy, \quad . \quad . \quad (2.44)$$

while (2.23) becomes replaced by

$$\sigma \bar{U} = \kappa g \bar{Z}, \quad 2\omega \bar{U} = -g \frac{dZ}{dy}, \quad . \quad . \quad (2.45)$$

where  $\bar{Z}$ ,  $\bar{U}$  are mean values of  $Z$ ,  $U$  across any transverse section at any time. We deduce that

$$\kappa^2 = \sigma^2 / g \bar{h}. \quad . \quad . \quad . \quad . \quad (2.46)$$

### 3. Transverse Current.

In this section we restrict our consideration to cases in which  $Z$  remains positive across the channel.

Equation (2.26) may be written in the form

$$\sigma^2 / \kappa^2 = gh_1, \quad . \quad . \quad . \quad . \quad (3.11)$$

where

$$h_1 = \int_{a_1}^{a_2} hZe^{-\frac{2\omega}{\sigma}\kappa y} dy \bigg/ \int_{a_1}^{a_2} Ze^{-\frac{2\omega}{\sigma}\kappa y} dy. \quad (3.12)$$

We deduce that the value of  $h_1$  will lie between the greatest and least values of  $h$ .

Equation (2.25) shows that if there is a shelving beach at  $y=a_1$  there will be a neighbouring region over which  $V$  is positive, while (2.25) and (2.26) together show that if there is a shelving beach at  $y=a_2$  there will be a neighbouring region over which  $V$  is negative. We deduce that if there is a shelving beach on either side of the channel, there will be a neighbouring region over which at a quarter period before high water the current is directed towards the shore. This is *Airy's Rule* (*l. c.* § 362), though his argument seems to depend on his erroneous result and he took no account of the Earth's rotation.

If there is a shelving beach at both sides of the channel, there must be at least two values of  $y$  for which  $h=h_1$ . The simplest natural case arises when there are only two such values of  $y$ , say  $y_1, y_2$ . In this case

$$hVe^{-\frac{2\omega}{\sigma}\kappa y}$$

will increase from zero at  $y=a_1$  to a maximum at  $y=y_1$ , then decrease to a minimum at  $y=y_2$ , and finally increase to zero at  $y=a_2$ . It follows that for a certain value of  $y$ , say  $y_0$ , between  $y_1$  and  $y_2$ ,  $V$  will change sign and that for  $a_1 < y < y_0$ ,  $V$  will be positive, while for  $y_0 < y < a_2$ ,  $V$  will be negative (*cf.* fig. 1). On either side of  $y=y_0$  along any section the transverse current at any time preserves the same sign and this sign changes at  $y=y_0$ . A quarter period before high water the current is directed towards the corresponding shore.

#### 4. Parabolic Section.

We now restrict our consideration to the parabolic section given by

$$h = h_0(1-y^2/a^2), \quad \dots \dots (4.1)$$

$h_0$  and  $a$  being constants, so that  $a_1 = -a$ ,  $a_2 = a$ .

We deduce

$$h = \frac{2}{3}h_0,$$

so that the narrow sea theory gives

$$\kappa^2 = \frac{3}{2}\sigma^2/gh_0 \quad \dots \dots (4.2)$$

by (2.46).



Taking now the *special case*  $\sigma = 2\omega$ , we deduce from (2.33)

$$\frac{\tanh 2\kappa a}{2\kappa a} = \frac{1}{1 + 2\sigma^2 a^2 / gh_0} \quad \dots \quad (4.31)$$

If  $a = 100$  km.,  $h_0 = 100$  m.,  $\sigma = 0.0014$  rad./sec. (semi-diurnal tides), we find  $\sigma^2 a^2 / gh_0 = 0.2$ .

The second column of the Table shows the ratio of  $\kappa^2$  as given by (4.31) to its value as given by the narrow sea theory.

$\frac{\sigma^2 a^2}{gh_0}$	$\kappa^2 / \frac{3}{2} \frac{\sigma^2}{gh_0}$	$1 + \frac{2}{5} \frac{\sigma^2 a^2}{gh_0}$
·1 .....	1.04	1.04
·2 .....	1.09	1.08
·3 .....	1.13	1.12
·4 .....	1.18	1.16
·5 .....	1.22	1.20
·6 .....	1.27	1.24
·7 .....	1.32	1.28
·8 .....	1.38	1.32
·9 .....	1.43	1.36
1.0 .....	1.49	1.40

For small values of  $\sigma^2 a^2 / gh_0$  we have, to the second order,

$$\kappa^2 = \frac{3}{2} \frac{\sigma^2}{gh_0} \left( 1 + \frac{2}{5} \frac{\sigma^2 a^2}{gh_0} \right) \quad \dots \quad (4.311)$$

The third column of the Table shows the ratio of the value of  $\kappa^2$  as given by (4.311) to that given by the narrow sea theory.

From (2.25) and (2.32) we deduce

$$\begin{aligned} & \frac{\sigma}{gh_0} hV \\ &= \frac{1}{2} \frac{e^{\kappa a}}{\kappa^2 a^2} \left[ \left\{ 1 + \frac{2\sigma^2 a^2}{gh_0} - \kappa^2(a^2 - y^2) - \kappa(a - y) \right\} \sinh \kappa(a + y) \right. \\ & \quad \left. + \{ \kappa^2(a^2 - y^2) - \kappa(a + y) \} \cosh \kappa(a + y) \right] \quad \dots \quad (4.32) \end{aligned}$$

From (2.31) and (2.32) we have

$$\begin{aligned} & \frac{\sigma}{gh_0} hU \\ &= \frac{1}{2} \frac{e^{\kappa a}}{\kappa^2 a^2} \left[ \left\{ 1 + \frac{2\sigma^2 a^2}{gh_0} + \kappa^2(a^2 - y^2) - \kappa(a - y) \right\} \sinh \kappa(a + y) \right. \\ & \quad \left. - \{ \kappa^2(a^2 - y^2) + \kappa(a + y) \} \cosh \kappa(a + y) \right] \quad \dots \quad (4.33) \end{aligned}$$

Figs. 1 and 2 show respectively the graphs of (4.32) and (4.33) from  $y = -a$  to  $y = a$ , for  $\sigma^2 a^2 / gh_0 = 0.1, 0.5, 1.0$ .

We notice that the line along which the transverse currents vanish is nearer to the left of the channel, looking in the direction of propagation of the wave, and that this lack of symmetry increases with the value of  $\sigma^2 a^2 / gh_0$ . When

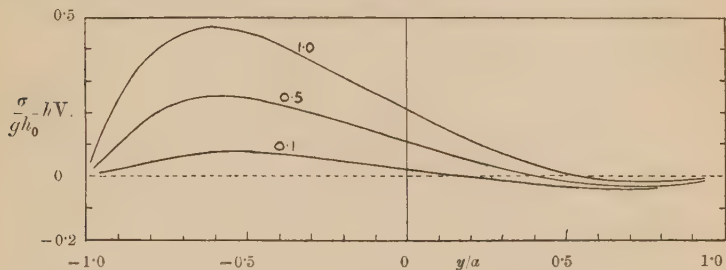


Fig. 1.

Showing distribution of transverse current across breadth of channel, looking in direction opposite to that of propagation of wave. Figures on curves are corresponding values of  $\sigma^2 a^2 / gh_0$ .

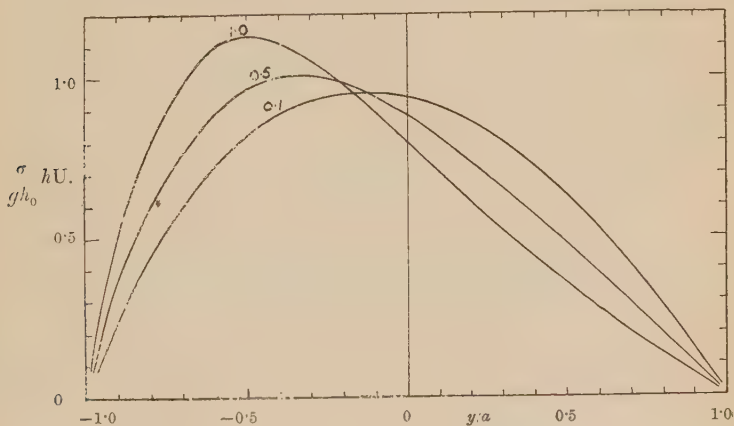


Fig. 2.

Showing distribution of longitudinal current across breadth of channel, looking in direction opposite to that of propagation of wave. Figures on curves are corresponding values of  $\sigma^2 a^2 / gh_0$ .

$\sigma^2 a^2 / gh_0 = 1$  the breadth of the left-hand region is relatively small and its currents are also relatively small. The ratio of transverse to longitudinal current reaches a maximum at the right side of the channel; its values for the cases of  $\sigma^2 a^2 / gh_0 = 0.1, 0.5, 1.0$  are 0.15, 0.35, 0.51 respectively.

Next let us suppose that the channel is *non-rotating* so that  $\omega=0$ , as would occur at the Equator.

On substituting into (2.28) from (4.1) we have

$$\frac{d}{dy} \left\{ \left( 1 - \frac{y^2}{a^2} \right) \frac{dZ}{dy} \right\} + \left\{ \frac{\sigma^2}{gh_0} - \kappa^2 \left( 1 - \frac{y^2}{a^2} \right) \right\} Z = 0. \quad (4.41)$$

For the symmetrical solution we assume the infinite series

$$Z = A_0 + A_2 \frac{y^2}{a^2} + \dots + A_n \frac{y^n}{a^n} + \dots, \quad (4.42)$$

where  $n$  is even, and on substituting we obtain

$$2A_2 + \left( \frac{\sigma^2 a^2}{gh_0} - \kappa^2 a^2 \right) A_0 = 0, \quad \dots \quad (4.43)$$

and

$$(n+2)(n+1)A_{n+2} - (n+1)nA_n + (\sigma^2 a^2 / gh_0 - \kappa^2 a^2) A_n = 0. \quad (4.44)$$

From (2.29) we require a value of  $\kappa$  which will make

$$\left( 1 - \frac{y^2}{a^2} \right) \frac{dZ}{dy} \rightarrow 0,$$

as  $y \rightarrow a$ , and to find this we may use the celebrated argument initiated by Laplace for an ocean covering the whole globe. We have from (4.44)

$$\frac{A_{n+2}}{A_n} = \frac{n}{n+2} + \frac{\kappa^2 a^2 - \sigma^2 a^2 / gh_0}{(n+2)(n+1)} - \frac{\kappa^2 a^2}{(n+2)(n+1)} \frac{A_n}{A_{n-2}}, \quad \dots \quad (4.441)$$

so that  $A_{n+2}/A_n$  tends either to 1 or 0 as  $n \rightarrow \infty$ .

In the former case we have, as the principal part,

$$\frac{A_{n+2}}{A_n} = \frac{n}{n+2},$$

so that the series (4.42) behaves like

$$\frac{1}{2} \frac{y^2}{a^2} + \frac{1}{4} \frac{y^4}{a^4} + \dots + \frac{1}{n} \frac{y^n}{a^n} + \dots$$

or

$$-\frac{1}{2} \log \left( 1 - \frac{y^2}{a^2} \right),$$

which is inadmissible as an expression for  $Z$ .

We therefore require those values of  $\kappa$  which make

$$\frac{A_{n+2}}{A_n} \rightarrow 0, \text{ as } n \rightarrow \infty, \quad \dots \quad (4.45)$$

On writing

$$\alpha_n = \frac{n}{n+2} + \frac{\kappa^2 a^2 - \sigma^2 a^2 / gh_0}{(n+2)(n+1)}, \quad \beta_n = \frac{\kappa^2 a^2}{(n+2)(n+1)}, \quad (4.46)$$

we have

$$\frac{A_n}{A_{n-2}} = \frac{\beta_n}{\alpha_n - A_{n+2}/A_n},$$

so that

$$\frac{A_2}{A_0} = \frac{\beta_2}{\alpha_2 - \frac{\beta_4}{\alpha_4 - \dots \frac{\beta_n}{\alpha_n - \dots}}}$$

on the assumption (4.45). But  $A_2/A_0 = \alpha_0$ , so that

$$\alpha_0 - \frac{\beta_2}{\alpha_2 - \frac{\beta_4}{\alpha_4 - \dots \frac{\beta_n}{\alpha_n - \dots}}} = 0, \quad . \quad . \quad (4.47)$$

$n$  being even, and this is the equation for the possible values of  $\kappa$ .

With  $\sigma^2 a^2 / gh_0$  small, we have as a first approximation to the lowest real root of (4.47)

$$\kappa^2 = \frac{3}{2} \sigma^2 / gh_0, \quad . \quad . \quad . \quad (4.471)$$

as in the narrow sea theory. As the next approximation to the lowest real root, we have

$$\kappa^2 = \frac{3}{2} \frac{\sigma^2}{gh_0} \left( 1 + \frac{1}{30} \frac{\sigma^2 a^2}{gh_0} \right), \quad . \quad . \quad (4.472)$$

which shows that the first approximation is very good.

Let us finally take the case of a *general rotation*. Equation (2.28) with (4.1) gives \*

$$a^2 \frac{d}{dy} \left\{ \left( 1 - \frac{y^2}{a^2} \right) \frac{dZ}{dy} \right\} + \left\{ \frac{\sigma^2 a^2 - 4\omega^2 a^2}{gh_0} - \kappa^2 (a^2 - y^2) - \frac{4\omega}{\sigma} \kappa y \right\} Z = 0. \quad (4.51)$$

Into this equation let us substitute the finite series

$$Z = A_0 + A_1 \frac{y}{a} + A_2 \frac{y^2}{a^2} + \dots + A_n \frac{y^n}{a^n} + \dots + A_m \frac{y^m}{a^m}. \quad (4.52)$$

\* The author has learnt that Dr. G. R. Goldsbrough examined this problem some years ago.





of  $y^m/a^m$ . We then see that (4.52) is a solution of (4.51) modified by the addition of

$$\left\{ \kappa^2 a^2 A_{m-1} - \frac{4\omega}{\sigma} \kappa a A_m \right\} \frac{y^{m+1}}{a^{m+1}} + \kappa^2 a^2 A_m \frac{y^{m+2}}{a^{m+2}} \quad (4.54)$$

to the right-hand side, and that the boundary conditions,

$$\left(1 - \frac{y^2}{a^2}\right) \left(\frac{dZ}{dy} + \frac{2\omega}{\sigma} \kappa Z\right) \rightarrow 0,$$

as  $y \rightarrow \pm a$ , are also satisfied.

Now the vanishing of the coefficient of  $y^n/a^n$  shows that after  $n$  reaches a certain value  $|A_{n+2}|$  is less than the greatest of

$$|A_{n-2}|, |A_{n-1}|, |A_n|,$$

and then the vanishing of the coefficients of  $y^{m-1}/a^{m-1}$  and  $y^m/a^m$  shows that as  $m \rightarrow \infty$

$$A_{m-1}, A_m \rightarrow 0.$$

We therefore see that, by taking  $m$  large enough, we can, with the choice of  $\kappa$  we have indicated, make (4.52) as near a solution of (4.51) as we please.

The equation for the possible values of  $\kappa$  is

$$\begin{vmatrix} \left(\kappa^2 - \frac{\sigma^2 - 4\omega^2}{gh_0}\right) a^2, & 0 & , & -2 & , & \dots \\ \frac{1}{2.1} \frac{4\omega}{\sigma} \kappa a & , & 1 + \frac{1}{2.1} \left(\kappa^2 - \frac{\sigma^2 - 4\omega^2}{gh_0}\right) a^2, & 0 & , & \dots \\ -\frac{1}{3.2} \kappa^2 a^2 & , & \frac{1}{3.2} \frac{4\omega}{\sigma} \kappa a & , & 1 + \frac{1}{3.2} \left(\kappa^2 - \frac{\sigma^2 - 4\omega^2}{gh_0}\right) a^2, & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{vmatrix} = 0. \quad (4.55)$$

If  $\sigma$  and  $\omega$  are of the same order and  $\sigma^2 a^2 / gh_0$  may be regarded as small, we have, to the second order,

$$\kappa^2 = \frac{3}{2} \frac{\sigma^2}{gh_0} \left\{ 1 + \frac{\sigma^2 + 4\omega^2}{30gh_0} a^2 \right\}, \quad \dots \quad (4.551)$$

which includes (4.311) and (4.472) as particular cases.

L. *A Modification of Rankine's Theory of Earth Pressures on Retaining Walls.* By WILLIAM J. WALKER, Ph.D., University College, Dundee \*.

OF the two principal theories of earth pressure, Rankine's and Coulomb's, the general tendency in favour of the latter is strikingly exemplified by the many "wedge" theories, all modifications of Coulomb's, which have been introduced by various authorities. This has been largely due to the generally excessive values obtained, by calculation from Rankine's formula, for the pressure on a vertical wall,

$$P = \frac{1}{2}wh^2 \cos \theta \left\{ \frac{\cos \theta - \sqrt{\cos^2 \theta - \cos^2 \phi}}{\cos \theta + \sqrt{\cos^2 \theta - \cos^2 \phi}} \right\} \\ = \frac{1}{2}wh^2 K, \dots \dots \dots (1)$$

where  $\theta$  is the angle of surcharge  
and  $\phi$  is the angle of repose,

the direction of  $P$  being parallel to the surface slope.

On the other hand, the application of the somewhat cumbersome Coulomb formula,

$$P = \frac{1}{2}wh^2 \frac{\sin^2 (\delta - \phi)}{\sin^2 \delta \sin^2 (\delta + z)} \left\{ 1 + \sqrt{\frac{\sin (z + \phi) \sin (\phi - \theta)}{\sin (\delta + z) \sin (\delta - \theta)}} \right\}$$

[where  $\theta$  and  $\phi$  are as before,  $\delta$  is angle which wall makes with vertical, and  $z$  is angle which resultant  $P$  makes with wall], or one of its many modifications, gives, in general, pressures which are more in agreement with results relating to the particular problem which may be under review. For a non-vertical wall, of course, Rankine's formula requires the addition or subtraction of the thrust due to the weight of the triangular prism of earth between the vertical and either the face or back of the wall according to the direction of inclination.

There is no doubt, however, that the existence of so many "wedge" theories, derived from the parent theory of Coulomb, indicates a lack of generality in the method. In particular cases, this or that wedge theory may be capable of giving closely approximate results to actual practical values, but none of them alone appear comprehensive enough to cover the wide diversity of earth-pressure problems which

\* Communicated by the Author.

may require solution. To the writer's mind, the main objection to the wedge type of theory, apart from the fictitious "plane of cleavage" which it postulates, is the implicit neglect of the extent of the supporting mass of earth beyond the wedge.

Rankine's theory follows more orthodox and fundamental lines, and it is more than probable that the lack of sufficient experimental data is all that prevented him from introducing the necessary correctives to his preliminary assumptions. In the derivation of his formula he assumed that the granular earth material

- (a) possessed an indefinitely extended upper surface, and
- (b) was incompressible.

Superficially, these two assumptions appear to be valid enough to give a formula capable of fairly general application. The modification which, in the light of all the data available, appears to be required in his theory lies in the abolition of the assumption of an infinitely extended surface. The writer here proposes to introduce this modification to Rankine's theory, and then to show, by application to specific tests, that the modified theory is capable of general application, besides possessing a more rational foundation than any wedge theory.

Two of the consequences of Rankine's assumption of an infinitely extended surface are that the vertical pressure and its conjugate for the granular material must vary directly as the depth, and that the centre of pressure on any plane rectangular surface, partially immersed in the material, must lie at two-thirds the depth of the plane from the surface of the material. These two results are at variance with all experience of earth pressures.

Taking, then, as the point of departure from Rankine's theory the assumption of a finitely extended surface, assume that sand or other granular material is contained in a cylinder of any peripheral form with vertical walls. The pressure  $p$ , at any depth, taken parallel to the surface slope, is given, in terms of the vertical pressure,  $q$  by

$$p = qK,$$

where  $K$  denotes the same expression as it does in (1).

Considering now the equilibrium of a cross-sectional element of the cylinder of thickness  $dc$  in the vertical direction, the section being taken parallel to the surface

slope, the upward force of friction supporting the element is given by

$$F = L_1 dx p \tan \phi \cos \theta,$$

where  $L_1$  is the periphery of the element, and the assumption is made that the friction between the wall and the granular material is the same as the internal friction of the material. Evidently, therefore, the upward intensity of pressure over the cylindrical cross-section of the element, due to this friction on the walls, may be written

$$\frac{F}{A} = \frac{L dx p \tan \phi}{A} = kq dx, \quad . \quad . \quad . \quad (2)$$

where  $L$  and  $A$  are the periphery and cross-sectional area respectively of the cylinder for a horizontal section, and  $k$  is a constant depending on the geometrical form of the cylinder, the angle of repose  $\phi$ , and the angle of surcharge  $\theta$ , and is given by

$$k = \frac{KL \tan \phi}{A}.$$

The equation of equilibrium of the element may therefore be written

$$dq = w dx - kq dx, \quad . \quad . \quad . \quad (3)$$

where  $w$  is the specific weight of the granular material. If the cylindrical mass carries a load  $W$  on its surface, the solution of (3) gives, for the pressure intensity  $q$  at any depth  $h$ , the equation

$$q = \frac{w}{k} \left\{ 1 - e^{-kh} \left( 1 - \frac{kW}{wA} \right) \right\}.$$

Writing

$$c = 1 - \frac{kW}{wA},$$

the resultant pressure  $P$  on unit width of wall is given by

$$\begin{aligned} P &= \frac{wK}{k} \int_0^h (1 - ce^{-kh}) dh \\ &= \frac{wA}{L \tan \phi} \left\{ h + \frac{c}{k} (e^{-kh} - 1) \right\}, \quad . \quad . \quad (4) \end{aligned}$$

and is parallel to the surface slope.

The foregoing analysis has been developed in all its generality without specifying any particular form of boundary

wall. In practice, however, these invariably form plane surfaces, and attention will now be confined to these. It should be observed that, although in general there may not be boundary wall on all sides of the mass of granular material, nevertheless at such points where no boundary wall exists the material will take up its natural angle of repose, and the assumption of a vertical boundary wall through the top edge of the natural bank thus formed fulfils the statical conditions of the problem.

Since the overturning moment on a wall is just as important a factor in design as the resultant pressure, it is necessary to determine the centre of pressure of the wall—i. e., the point at which the resultant pressure acts. The equation to determine the depth  $H$  of the centre of pressure of a plane vertical wall is given by

$$H \Sigma p \, ds = \Sigma hp \, ds,$$

where  $ds$  is the small surface element at which  $p$  acts.

But

$$p = \frac{wK}{k} (1 - ce^{-kh}).$$

∴ For a vertical line element of wall

$$H [\Sigma dh - c \Sigma e^{-kh} dh] = [\Sigma h dh - c \Sigma he^{-kh} dh].$$

$$\therefore H \left[ \int_0^h dh - c \int_0^h e^{-kh} dh \right] = \left[ \int_0^h h dh - c \int_0^h he^{-kh} dh \right],$$

which gives

$$H = \frac{\frac{h^2}{2} + \frac{c}{k^2} [\{e^{-kh}(kh+1) - 1\}]}{h + \frac{c}{k}(e^{-kh} - 1)},$$

where  $h$  is the covered depth of the wall.

Expressions (4) and (5), therefore, are the modified formulæ for obtaining the resultant pressure, the centre of pressure, and therefore the overturning moment on a retaining wall. Applying these to experiments carried out by Prof. A. R. Fulton\*, the following table has been drawn up, the experimental results in which correspond

\* "Overturning Moment on Retaining Walls," Proc. I. C. E. ccix, part i. (1919-20).

to Table I. of Prof. Fulton's paper. The values of  $K$  and  $k$  were calculated from the given data.

Material.		No surcharge.—Wall vertical.								
		Gravel.			Sand.			Earth.		
<i>h</i> feet .....		3	5	7	3	5	7	3	5	7
Experimental moment—lb. feet .....		91	480	1092	78	364	936	60	300	728
Calculated moments.	{ Wedge formula ...	93	431	1182	75	345	948	57	262	719
	{ Rankine's „ ...	122	560	1537	99	457	1255	77	355	973
	{ Modified „ ...	97	462	1170	84	378	942	65	300	758

It will be observed that the calculated values obtained from the modified formula give a maximum excess of calculated pressure of about 8 per cent. and a maximum deficit of 5 per cent., whereas the wedge formula gives corresponding maxima of excess and deficit of 8 and 12 per cent. respectively.

From the foregoing, therefore, it is clear that Rankine's theory of earth pressures, fundamental as it is in character, is perfectly capable, when modified in the manner indicated, of giving results closely approximate to those to be expected in practice.

LI. *On an Application of the Periodogram to Wireless Telegraphy.* By C. R. BURCH, B.A., and J. BLOEMSMA, M.N.I.R.E.\*

SUMMARY.

THIS paper discusses the response of a wireless receiver to morse signals and also to atmospherics, in terms of the periodogram of the pulse, and the resonance curve of the receiver. The effect of heterodyne detection is examined, and the shape of the resonance curve of the ideal receiver is discussed.

The relative merits of open and closed antennæ are determined, and a weakness of the limiter selector-method of reception is indicated.

I. INTRODUCTION.

IT is often said that a non-periodic oscillation "contains all frequencies." It is the object of this paper to assign a definite quantitative interpretation to this statement, and to draw therefrom certain conclusions as to the behaviour of resonant systems under impulse excitation.

\* Communicated by Dr. W. H. Eccles, F.R.S.



For a fuller mathematical treatment of the same subject, of very rigid nature, reference should be made to the work of Dr. A. Koerts, 'Atmosphärische Störungen in der drahtlosen Nachrichtenübermittlung,' to which the attention of the authors has been drawn since the completion of this paper, which is now offered in view of its different extension into detail, and its simpler attack.

Let the non-periodic oscillation be given by  $E=f(t)$  from  $t=0$  to  $t=\infty$ , where the function  $f$ , finite and single-valued for all values of  $t$ , and vanishing at  $t=\infty$ , is restricted to a type expandible as a Fourier series.

An example of sufficient conditions is as follows:—

The function  $f$  should have only a finite number of maxima, minima, and discontinuities in any finite range of  $t$ , and it should vanish at  $t=\infty$  to a higher order than  $t^{-1}$ .

The Periodogram of  $E, =f(t)$ , a complex function,  $X_q, =(a_q + ib_q)$  of  $f(t)$  and the parameter  $q$ , defined as

$$X_q = \int_0^{\infty} f(t) \cdot \epsilon^{iqt} \cdot dt,$$

where  $\epsilon$  is the base of natural logarithms and  $i \equiv \sqrt{-1}$ , will then exist as the limit of a sum.

$X_q dq$  represents in magnitude and phase  $\pi$  times the contribution to  $E$  arising from pulsataces  $q$  to  $q + dq$ , for  $E$  may be written as the real part of

$$\frac{1}{\pi} \int_0^{\infty} X_q \epsilon^{-iqt} = dq. \quad . \quad . \quad . \quad . \quad (1)$$

$|X_q|^2 \cdot dq, =(a_q^2 + b_q^2)$ , is  $\pi$  times the contribution to  $\int_0^{\infty} E^2 dt$  due to pulsataces  $q$  to  $q + dq$ , and

$$\int_0^{\infty} E^2 dt = \frac{1}{\pi} \int_0^{\infty} |X_q|^2 \cdot dq. \quad . \quad . \quad . \quad . \quad (2)$$

The validity of (1) and (2) follows from the fact that they are the limiting forms of the Fourier treatment of the function  $f$ , over a finite time, as that time is made indefinitely great.

The definition of  $X_q$  determines it uniquely in terms of  $f(t)$ , and it follows from (2) that the periodogram determines the function uniquely, for if two different functions had the same periodogram, a difference-function would exist having  $X_q$  zero for all values of  $q$ .

It would then have  $\int_0^{\infty} E^2 dt$  zero, and therefore  $E$  zero

for all time. In fact, the two supposedly different functions are identical.

The subject has been treated by Lord Rayleigh, "Remarks concerning Fourier's Theorem as applied to Physical Problems," *Phil. Mag.* xxiv. pp. 864-869 (1912). It is there shown that smoothing the function  $f$  annuls  $X_q$  for large values of  $q$ , while smoothing  $X_q$  as a function of  $q$  annuls the equivalent function,  $f$ , for values of  $t$  numerically great.

In wireless problems  $E$  may represent any electrical quantity (electric force, current, charge). In using the periodogram to deduce from the form of  $f(t)$  the behaviour of any of these quantities ( $Q$ ) in a resonant system, it is necessary to consider also a similar complex function,  $Y_{q,(Q,E)} = x_q + iy_q$ , a function of the circuit constants and the parameter  $q$ .

We contemplate only systems having for every possible free vibration a finite, positive, damping exponent. For such systems,  $Y_q(Q, E)$  is so defined that if  $E$  were periodic, and equal to the real part of  $E_0 e^{iqt}$ ,  $Q$  in the branch under examination (not necessarily that in which  $E$  is present) would, after infinite time, be the real part of  $Y_q E_0 e^{iqt}$ .

Thus in a simple LRC circuit, if  $E$  is the induced voltage, and we wish to examine the current ( $Q$ ), we write

$$Y_q = \frac{iqC}{1 - q^2 LC + iqCR}.$$

In the case of  $E = f(t)$ , ( $Q$ ) may be written as the real part of

$$\frac{1}{\pi} \int_0^\infty \epsilon^{-iqt} X_q \cdot Y_q \cdot dq. \quad . \quad . \quad . \quad . \quad (3)$$

This form is intractable analytically, and is unsuitable for numerical calculation in the case when the mathematical expressions represent only approximately the exact physical conditions—a difficulty met with in many of the formulæ of mathematical physics.

Though it may be present to such an extent as to render integral (3) as it stands, devoid of meaning, the less general form

$$\int_0^\infty Q^2 dt = \frac{1}{\pi} \int_0^\infty |X_q|^2 \cdot |Y_q|^2 \cdot dq \quad . \quad . \quad . \quad (4)$$

will still afford a basis for numerical computation.

The validity of (3) and (4) follows in the same way as that of (1) and (2), for they are the limiting forms of the Fourier treatment, over the range  $-t_1$  to  $+t_1$  of a function

zero from  $-t_1$  to 0, and equal to  $f(t)$  from  $t=0$  to  $t=+t_1$ , as  $t_1$  is made indefinitely great. In calculating  $Q$  in that case, it is only necessary to take account of the particular integral (forced vibration), for the complementary function (free vibration) may be regarded as having died out during the interval  $-t_1$  to zero. Note that  $\int_0^\infty Q^2 dt$  is the inte-

grated response of any square-law detector, *e. g.* a crystal, or valve detector without heterodyne, or the total heat generated in a resistance, and hence the throw of a thermocouple-galvanometer.

A general result may be deduced from (3). If two LRC assemblies have  $Y_q$  identical for a particular branch, for all values of  $q$ ,  $Q$  in that branch, due to a pulse  $E$ , is in each case identically the same function of  $t$ .

In particular, for two simple circuits,  $L_1 R_1 C_1$ ,  $L_2 R_2 C_2$ , mutual inductance  $M$ , the current produced in (2) due to the induced voltage  $E$  in (1) is identically that produced in (1) by the pulse  $E$  induced in (2), whatever may be the values of  $L_1 R_1 C_1$ ,  $L_2 R_2 C_2$ , and  $M$ .

In the case of three inductively coupled circuits, a voltage pulse in the first produces in the last exactly that current produced in the first by the same pulse acting in the last.

The current in the final element of a chain of infinitely weakly coupled circuits is unaltered in form by changing the order of the circuits, and keeps its magnitude if the (infinitesimal) product of the mutual inductances remains the same.

We have seen that  $\int_0^\infty Q^2 dt$  may be regarded as a measure of the response of a wireless receiver. We shall use (4) to compute the response to the pulses used to represent atmospherics, and also to pulses of the very special, approximately-periodic type called morse signals. It is therefore necessary to examine  $X_q$  as a function of  $q$  for several types of pulse.

## II. PERIODOGRAMS OF COMMON ANALYTICAL PULSE-FORMS.

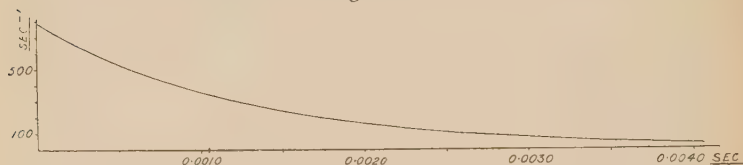
As a basis of comparison of different types of pulse,  $E=f(t)$ , we shall mention  $\int_0^\infty E dt$  and  $\int_0^\infty E^2 dt$ , as, according to circumstances, it may be of interest to compare equal charges, or equal energies.

(1) The Aperiodic pulse,  $E = E_0 e^{-\alpha t}$ , lasting from  $t = 0$  to  $t = +\infty$ .

$$\int_0^\infty E dt = \frac{E_0}{\alpha}, \quad \int_0^\infty E^2 dt = \frac{E_0^2}{2\alpha}.$$

$$|X_q|^2 = \frac{E_0^2}{(\alpha^2 + q^2)} \text{ vanishing for } q = \infty \text{ as } q^{-2}. \quad (\text{Figs. 1 \& 11.})$$

Fig. 1.



$$\frac{E}{C} = 788 e^{-788t} \text{ sec}^{-1}, \quad C = \int_0^\infty E dt = \text{constant} \left( \frac{\text{volt}}{\text{metre}} \text{ sec.} \right).$$

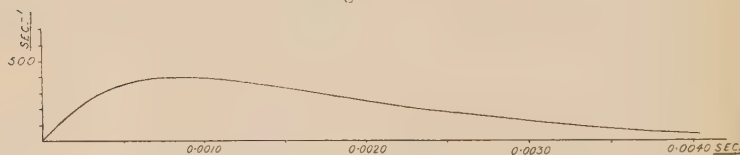
$$\alpha = 250\pi = 788.$$

(2)  $E = E_0(\epsilon^{-\alpha t} - \epsilon^{-2\alpha t})$  from  $t = 0$  to  $t = +\infty$ .

$$\int_0^\infty E dt = \frac{E_0}{2\alpha}, \quad \int_0^\infty E^2 dt = \frac{E_0^2}{12\alpha}.$$

$$|X_q|^2 = \frac{\alpha^2 E_0^2}{(\alpha^2 + q^2)(4\alpha^2 + q^2)} \text{ vanishing for } q = \infty \text{ as } q^{-4}. \quad (\text{Figs. 2 \& 11.})$$

Fig. 2.



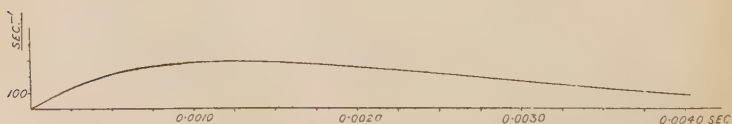
$$\frac{E}{C} = 1576 (\epsilon^{-788t} - \epsilon^{-1576t}) \text{ sec}^{-1}.$$

(3)  $E = E_0 \alpha t e^{-\alpha t}$  from  $t = 0$  to  $t = +\infty$ .

$$\int_0^\infty E dt = \frac{E_0}{\alpha}, \quad \int_0^\infty E^2 dt = \frac{E_0^2}{4\alpha}.$$

$$|X_q|^2 = \frac{\alpha^2 E_0^2}{(\alpha^2 + q^2)^2} \text{ vanishing for } q = \infty \text{ as } q^{-4}. \quad (\text{Figs. 3 \& 11.})$$

Fig. 3.



$$\frac{E}{C} = 788^2 t \cdot e^{-788t} \text{ sec}^{-1}.$$

(4) The isolated half-sine wave,

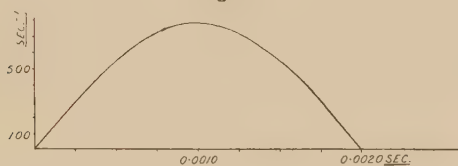
$$E = E_0 \sin pt \text{ from } t=0 \text{ to } t=\pi/p.$$

$$\int_0^\infty E dt = \frac{2E_0}{p}, \quad \int_0^\infty E^2 dt = \frac{E_0^2 \cdot \pi}{2p},$$

$$|X_q|^2 = \frac{4p^2 E_0^2 \cos^2 \frac{\pi}{2} q/p}{(q^2 - p^2)^2} \text{ vanishing for } q = \infty \text{ as } q^{-4}.$$

(Figs. 4 & 11.)

Fig. 4.



$$\frac{E}{C} = 788 \sin 1576t. \text{ sec}^{-1}. \quad p = 500\pi = 1576.$$

(5) The "sensibly innocuous" pulse of Moullin\*,

$$E = E_0 (\sin pt - \frac{1}{3} \sin 3pt) \text{ from } t=0 \text{ to } t=\pi/p.$$

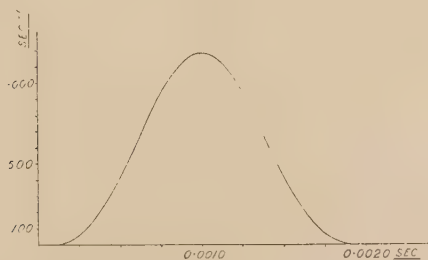
At both these times, all the derivatives up to the third are zero.

$$\int_0^\infty E dt = \frac{16}{9} \frac{E_0}{p}, \quad \int_0^\infty E^2 dt = \frac{14\pi}{27p} E_0^2.$$

$$|X_q|^2 = \frac{256p^6 E_0^2 \cos^2 \frac{\pi}{2} q/p}{(q^2 - p^2)^2 (q^2 - 9p^2)^2} \text{ vanishing for } q = \infty \text{ as } q^{-8}.$$

(Figs. 5 & 11.)

Fig. 5.



$$\frac{E}{C} = \frac{9}{16} = 1576 (\sin 1576t - \frac{1}{3} \sin 4728t).$$

\* J. I. E. E. No. 328, vol. lxii. p. 356, April 1924. E. B. Moullin, M.A., "Atmospherics and their effect on Wireless Receivers."



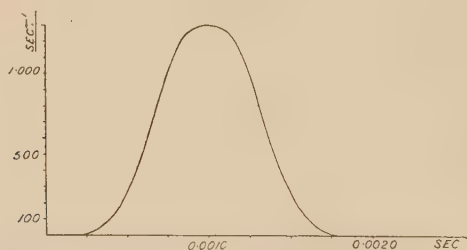
(6)  $E = E_0(\sin pt - \frac{1}{2} \sin 3pt + \frac{1}{10} \sin 5pt)$  from  $t=0$  to  $t=\pi/p$ . At both these times, all the derivatives up to the 5th are zero.

$$\int_0^\infty E dt = \frac{128}{75} \frac{E_0}{p}, \quad \int_0^\infty E^2 dt = \frac{689\pi}{1500} \frac{E_0^2}{p}.$$

$$|X_q|^2 = \frac{384^2 \cdot p^{10} \cdot E_0^2 \cdot \cos^2 \frac{\pi}{2} q/p}{(q^2 - p^2)^2 (q^2 - 9p^2)^2 (q^2 - 25p^2)^2} \text{ vanishing for } q = \infty \text{ as } q^{-12}.$$

(Figs. 6 &amp; 11.)

Fig. 6.



$$\frac{E}{C} = 925(\sin 500\pi t - \frac{1}{2} \sin 1500\pi t + \frac{1}{10} \sin 2500\pi t).$$

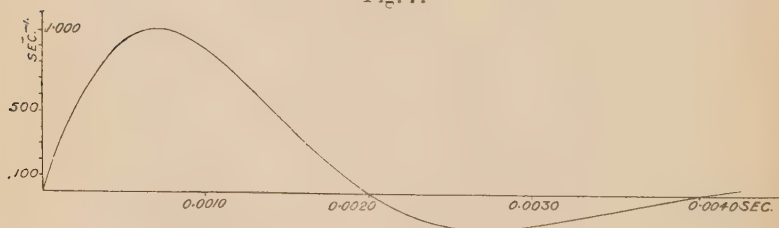
(7) The exponentially damped sine wave  $E = E_0 e^{-\alpha t} \sin pt$ , from  $t=0$  to  $t=+\infty$ .

$$\int_0^\infty E dt = \frac{p}{p^2 + \alpha^2} E_0, \quad \int_0^\infty E^2 dt = \frac{p^2 E_0^2}{4\alpha(p^2 + \alpha^2)}.$$

$$|X_q|^2 = \frac{p^2 E_0^2}{(\alpha^2 - q^2 + p^2)^2 + 4\alpha^2 q^2} \text{ vanishing for } q = \infty \text{ as } q^{-4}.$$

(Fig. 7.)

Fig. 7.



$$\frac{E}{C} = 1.25 \times 500\pi \times e^{-250\pi t} \sin 500\pi t \text{ sec}^{-1}.$$

This function is similar to the resonance curve of an LRC circuit, having a maximum at  $q=p$ . Writing  $\alpha = \delta/2\pi$ , the form of  $|X_q|^2$  is given near  $q=p$  when  $\delta < 1$ , by the

approximation

$$\frac{|X_{p+\Delta p}|^2}{|X_p|^2} \doteq \frac{\left(\frac{\delta}{2\pi}\right)^2}{\left(\frac{\Delta p}{p}\right)^2 + \left(\frac{\delta}{2\pi}\right)^2}, \quad \dots \quad (5)$$

also

$$\frac{|X_p|^2}{\int_0^\infty E^2 dt} \doteq \frac{1}{\alpha} = \frac{2\pi}{\delta p}$$

—a result strongly suggesting the damped-wave resonance formulæ of Bjerknes, Brandes, Mandelstam and Papalexi and others. We shall return to this later.

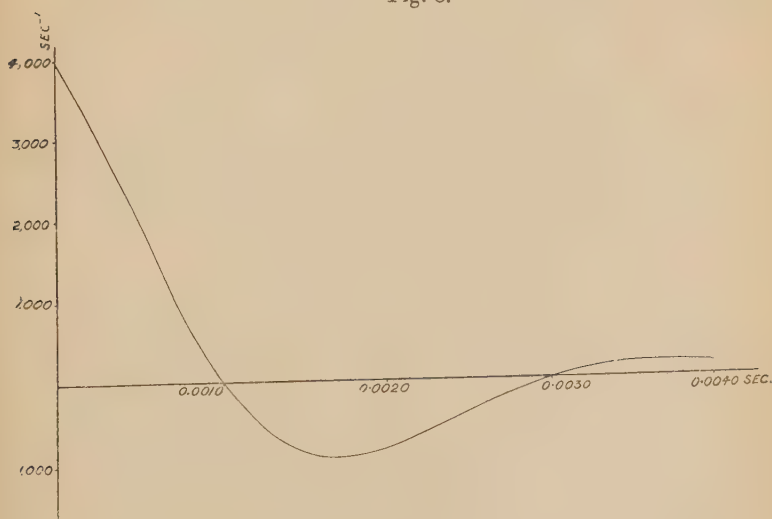
(8) The exponentially damped cosine wave  $E = E_0 e^{-\alpha t} \cos pt$  from  $t=0$  to  $t=+\infty$ .

$$\int_0^\infty E dt = \frac{\alpha}{p^2 + \alpha^2} E_0, \quad \int_0^\infty E^2 dt = \frac{2\alpha^2 + p^2}{4\alpha(p^2 + \alpha^2)} E_0^2.$$

$$|X_q|^2 = \frac{(\alpha^2 + q^2) E_0^2}{(\alpha^2 - q^2 + p^2)^2 + 4\alpha^2 q^2} \text{ vanishing for } q = \infty \text{ as } q^{-2}. \quad (\text{Fig. 8.})$$

The same equation (5) may be deduced.

Fig. 8.



$$\frac{E}{C} = 1250\pi \cdot e^{-250\pi t} \cdot \cos 500\pi t \cdot \text{sec}^{-1}.$$

{The ordinates are on half the scale of the other figs.}

(9) The linearly damped sine wave.

$$E = E_0(1 - \beta t) \sin pt \text{ lasting from } t=0 \text{ to } t=\beta^{-1}.$$

If we assume  $p = \pi m \beta$  ( $m$  half-oscillations)

$$\int_0^\infty E dt = \frac{E_0}{p}, \quad \int_0^\infty E^2 dt = E_0^2 \left[ \frac{2p^2 - 3\beta^2}{12\beta p^2} \right],$$

$$\text{which} \quad = E_0^2 \cdot \frac{8\pi^2 m^2 - 3}{24\pi m p} \div \frac{\pi m}{3p} \cdot E_0^2 \quad (m \gg 1).$$

$$|X_q|^2 = \frac{p^2 E_0^2}{(q^2 - p^2)^2} \left[ 1 - \frac{4pq \sin \frac{\pi m q}{p}}{(q^2 - p^2)} \cos \pi m \right. \\ \left. + \frac{8p^2 q^2}{(q^2 - p^2)^2} \left[ 1 - \cos \frac{\pi m q}{p} \cos \pi m \right] \right] \text{ vanishing}$$

for  $q = \infty$  as  $q^{-4}$ .

For

$$q = p, \quad \frac{|X_p|^2}{\int_0^\infty E^2 dt} = \frac{3}{2p} \cdot \frac{4\pi^2 m^2 + 1}{8\pi^2 m^2 - 3} \cdot \pi m, \quad \div \frac{3\pi m}{4p}.$$

For an exponentially damped sine-wave (7) the same quantity is  $2\pi/p\delta$ . Thus if two waves of types (9) and (7) have the same total energy,

$$\frac{|X_p|^2 \text{ linear}}{|X_p|^2 \text{ exponential}} = \frac{3m\delta}{8}.$$

The waves start alike if  $m\delta = 1$ .

Thus if the action of a spark-gap is to rise in resistance during the later stages of the oscillation in such a way as to produce linear damping, with the initial damping due to the circuit resistance, the ratio

$$\frac{\text{Energy density at Pulsatance}}{\text{Total Energy}}$$

is the same as if the spark-gap did not do this, but  $\delta$  were increased in the ratio 8 : 3.

(10) The infinitely short pulse ("high frequency ripple").

$$\text{Lt}_{\delta t=0} \text{ of } \int_0^{\delta t} E dt = I, \text{ and } E \text{ zero except from } t=0 \text{ to } t=\delta t.$$

$$\int_0^\infty E^2 dt \text{ is infinite.}$$

$|X_q|^2 = I^2$ . This type thus has a constant distribution over the whole spectrum, independent of frequency.

Periodograms of Typical Morse Signals.

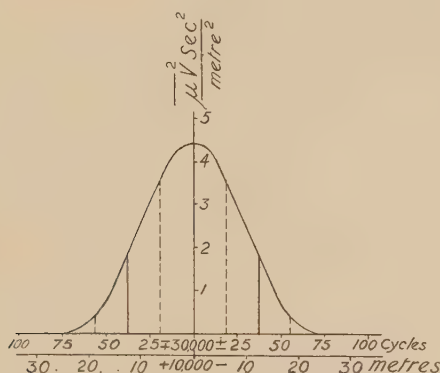
(11) One C.W. dot.

$$E = E_0 \sin pt \text{ from } t=0 \text{ to } t = \frac{2m\pi}{p}.$$

( $m$  complete oscillations).

$$|X_q|^2 = \frac{4p^2 E_0^2 \sin^2 \pi m q / p}{(q^2 - p^2)^2}, \quad |X_p|^2 = \frac{\pi^2 m^2}{p^2} E_0^2. \quad (\text{Fig. 9.})$$

Fig. 9.



Relative values of contained energy at different frequencies for an infinite succession of C.W. Dots.

Full drawn: synphased. Broken: antiphased.

$\lambda = 10,000$  metres. 400 oscillations per Dot (95 words per minute).

The curved line is the periodogram for one dot.

Maximum received field strength  $10 \mu V/\text{metre}$ .

(12) Two C.W. dots (synphased).

$$E = E_0 \sin pt, \quad \text{zero}, \quad E_0 \sin pt, \quad \text{from } t=0 \text{ to } t = \frac{2m\pi}{p},$$

$\frac{2m\pi}{p}$  to  $\frac{4m\pi}{p}$ ,  $\frac{4m\pi}{p}$  to  $\frac{6m\pi}{p}$  respectively, and zero before and after.

$$|X_q|^2 = \frac{16p^2 E_0^2}{(q^2 - p^2)^2} \sin^2 \frac{\pi m q}{p} \cos^2 \frac{2\pi m q}{p},$$

$$|X_p|^2 = \frac{4\pi^2 m^2}{p^2} E_0^2. \quad (\text{Fig. 12.})$$

(13) Two antiphased C.W. dots.

$E = E_0 \sin pt$  zero,  $-E_0 \sin pt$ , at the same times as above.

$$|X_q|^2 = \frac{16p^2 E_0^2}{(q^2 - p^2)^2} \sin^2 \frac{\pi m q}{p} \cdot \sin^2 2\pi m q/p, \quad |X_p|^2 = \text{zero.}$$

(Fig. 12.)

(14) An infinite succession of synphased C.W. dots.

$E = E_0 \sin pt$ , or zero, alternately with note pulsance,  $z = p/4m$ ,  $2m$  complete oscillations in a dot.

$$|X_{kz}|^2 = \frac{4p^2 E_0^2 \sin^2 k\pi/2}{(p^2 - k^2 z^2)^2}, \quad (\text{Fig. 9.})$$

in which  $k$  is a positive integer. The energy is reduced to that of one dot.

(15) An infinite succession of antiphased C.W. dots.

$E = E_0 \sin pt$ , zero,  $-E_0 \sin pt$ , zero, alternately.

Note pulsance  $z = p/4m$ ,  $2m$  complete oscillations in a dot.

$$|X_{kz}|^2 = \frac{16p^2 E_0^2 \sin^2 k\pi/2}{(p^2 - k^2 z^2)^2} \sin k\pi/4, \quad (\text{Fig. 9.})$$

where  $k$  is a positive integer. The energy is reduced to that of one dot. For this and the previous case  $|X_q|^2$  for values of  $q \neq kz$  is zero.

### *On the Repetition of a Pulse.*

Suppose the pulse  $E$  to occur  $n$  times at regular intervals (note pulsance  $z$ ). Let  ${}_1X_q$  be the periodogram of  $E = f(t)$ , occurring once.

Then  ${}_nX_q$ , that of

$$E = \underset{\substack{t=0 \\ \text{to } t=\infty}}{f(t)} + \underset{\substack{t=2\pi/z \\ \text{to } t=\infty}}{f\left(t - \frac{2\pi}{z}\right)} + \dots + \underset{\substack{t=\frac{2\pi(n-1)}{z} \\ \text{to } t=\infty}}{f\left(t - \frac{2\pi(n-1)}{z}\right)}$$

is given rigidly by

$${}_nX_q = {}_1X_q \left[ 1 + e^{2\pi i \frac{q}{z}} + e^{2\pi i \cdot \frac{2q}{z}} + \dots + e^{2\pi i \cdot \frac{(n-1)q}{z}} \right],$$

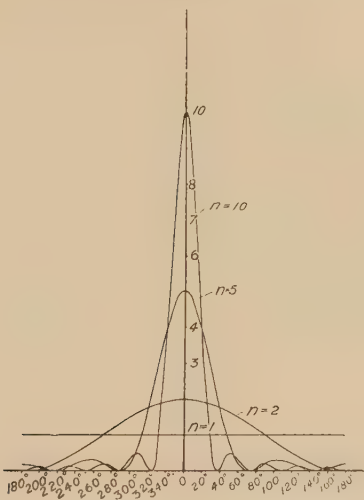
and it follows that

$$|{}_nX_q|^2 = |{}_1X_q|^2 \cdot \frac{\sin^2 n\pi q/z}{\sin^2 \pi q/z}.$$

The periodic curve  $\frac{\sin^2 n\pi q/z}{n \sin^2 \pi q/z}$  is plotted for various values of  $n$  in fig. 10. These curves, considered as multipliers, acting on  $|X_q|^2$ , show the effect of regular repetition of a

pulse, in concentrating the energy-density round those values of pulsance which are harmonics of the note-pulsance.

Fig. 10.



$$\frac{|nX_q|^2}{n|X_q|^2} = \frac{\sin^2 \pi q/2}{n \sin^2 \pi q/2} \text{ plotted against } q/90 \times 360^\circ.$$

Family of Curves for  $n=1, 2, 5, 10$ .

*On the Periodogram of a Pulse and that of its Envelope.*

If a pulse may be represented as  $\phi(t) \sin pt$  or  $\phi(t) \cos pt$ , we shall call  $\phi(t)$  the envelope of the pulse. There is a simple relation between the periodogram of a pulse,  $X_q$ , and that of its envelope  $\chi_q$ .

If  $X_q = a_q + ib_q$  and  $\chi_q = \alpha_q + i\beta_q$ , the following relations exist, for

$$f(t) = \phi(t) \sin pt,$$

$$a_q = \frac{1}{2}(\beta_{p+q} + \beta_{p-q}) \text{ and } b_q = \frac{1}{2}(\alpha_{p-q} - \alpha_{p+q}).$$

For

$$j(t) = \phi(t) \cos pt,$$

$$\alpha_q = \frac{1}{2}(\alpha_{p+q} + \alpha_{p-q}) \text{ and } \beta_q = \frac{1}{2}(\beta_{p+q} + \beta_{p-q}).$$

Now in morse signal pulses such as the C.W. dot, the exponentially and linearly damped sine wave, for values of  $q$  near to  $p$ ,  $\alpha_{p+q}$  and  $\beta_{p+q}$  are  $< \alpha_{p-q}$  and  $\beta_{p-q}$ , therefore approximately

$$|X_{p+\Delta p}| = \frac{1}{2} |\chi_{\Delta p}|.$$



Thus the periodogram of the envelope determines the shape of the principal peak in that of the pulse. It gives a generalization of the so-called "side-bands" of a transmission.

If we apply this reasoning to a pulse of type (7) we have (see type (1)),

$$\frac{|X_{p+\Delta p}|^2}{|X_p|^2} = \frac{|\chi_{\Delta p}|^2}{|\chi_0|^2} = \frac{\alpha^2}{(\Delta p)^2 + \alpha^2} = \frac{\left(\frac{\delta}{2\pi}\right)^2}{\left(\frac{\Delta p}{p}\right)^2 + \left(\frac{\delta}{2\pi}\right)^2},$$

an elegant way to deduce Bjerknes' law.

### The General Type.

Let  $E=f(t)$  from  $t=0$  to  $t=\infty$ , and let  $f$  satisfy the conditions sufficient to warrant the validity of the Fourier development.

Consider the general integral

$$Z = \int_0^\infty f(t) \cdot \epsilon^{igt} \cdot dt.$$

Partial integration gives

$$\begin{aligned} Z &= \epsilon^{igt} \left( \frac{-i}{q} \right) \left[ f + \left( \frac{i}{q} \right) f' + \frac{i^2}{q^2} f'' + \dots + \left( \frac{i}{q} \right)^n f^n \right] \\ &\quad + \left( \frac{i}{q} \right)^{n+1} \int_0^\infty f^{n+1}(t) \cdot \epsilon^{igt} \cdot dt \\ &= \epsilon^{igt} \left[ \frac{-f}{D + iq} \right]_n(t) + \left( \frac{i}{q} \right)^{n+1} \int_0^\infty \epsilon^{igt} \cdot f^{n+1}(t) \cdot dt, \end{aligned}$$

where  $D$  denotes  $d/dt$ . The interpretation to be put on this form is that it must be expanded as a power-series in  $D$  which operates on  $f(t)$ . Insertion of the limits of 0 and  $\infty$  gives

$$X_q = \left[ \frac{-f}{D + iq} \right] (0).$$

When the function or a derivative shows discontinuities at  $t=t_1$ ,

$$X_q = \left[ \frac{-f}{D + iq} \right] (0) + \left[ \frac{-f}{D + iq} \right] (t_1 + 0) - \left[ \frac{-f}{D + iq} \right] (t_1 - 0).$$

Thus, in the case of a function continuous with all its derivatives from  $t=0$  to  $t=\infty$ , the periodogram is entirely determined by the function and its derivatives at  $t=0$ , being in fact

$$X_q = \frac{i}{q} \left[ f(0) + \left( \frac{i}{q} \right) f'(0) + \left( \frac{i}{q} \right)^2 f''(0) + \dots + \dots \right].$$

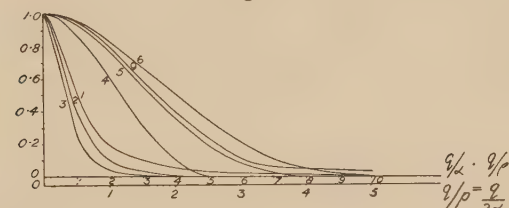
The series is generally found to be rapidly convergent with large values of  $q$ , and it is evident that the more of the earlier derivatives are zero, the higher is the order of  $q^{-1}$ , to which  $|X_q|$  is proportional, with infinite  $q$ .

### Approximate Pulse Forms.

It follows that if the form of a pulse is only approximately known (as, for instance, from an oscillogram), it will not be legitimate, having represented the pulse by an approximate mathematical expression, to deduce from that expression the behaviour of  $|X_q|$  with infinite  $q$ , and the values obtained for  $|X_q|$  will decrease in reliability as  $q$  is increased. We shall, however, find that in discussing the elimination of atmospheric pulses while receiving signals on any one frequency, the order of  $|X_q|$  with infinite  $q$  is unimportant.

$|X_q|^2$  for different types of pulse is plotted in figs. 1-6, 9, 11, 12, and  $|X_q|^2$  for great values of  $q$  is given in Table I.

Fig. 11.



$\frac{|X_q|^2}{C^2}$ , for different pulse forms (1, 2, 3, 4, 5, 6, 9)

based upon  $\int_0^\infty E dt = C = \text{Constant}$ .

As a basis for comparison  $\int_0^\infty E dt$  has been taken as constant ( $c$ ), and  $\alpha = p/2$ ,  $\beta = p/2$ .

It is clear that the principal features distinguishing the periodograms of pulses which might be used to represent atmospherics from those of the pulses used in wireless signalling are (1) that the principal maxima of the former occur at lower values of  $q$  than those of the latter; (2) that the principal maxima of the morse signals are very much more sharply defined.

In fact, while static may be said to "have all wave-lengths, though principally long ones," signals "on" a certain wave-length have all but a very small portion of their action concentrated near that wave-length.

We have now to consider  $X_q$  in conjunction with  $Y_q$ .

TABLE I.

Pulse No.	$E=f(t)$	$(X_q)^2, q=3 \times 10^4$ $(X_q)^2, q=3 \times 10^5$ $\lambda=10 \text{ km.}$ $\lambda=1 \text{ km.}$	
		unit: $\left(\frac{\text{volt. second}}{\text{metre}} 10^{-10}\right)^2$	
(1)	$E=E_0 e^{-at}$ $t=0 \text{ to } t=+\infty$ $a=0$ $E_0=1 \frac{\text{volt}}{\text{metre}}$		
Simple Discontinuity in E .....		$2.8145 \times 10^9$	$2.8145 \times 10^7$
(4)	$E=E_0 \sin pt$ $t=0 \text{ to } t=\pi/p$ $E_0=1 \frac{\text{volt}}{\text{metre}}$	$\frac{p}{2\pi} \approx \frac{500}{\text{sec.}}$ $p^2=10^7$	
Half Sine Wave .....		$1.2854 \times 10^6$	$1.2854 \times 10^2$
(5)	$E_0=E_0 (\sin pt - \frac{1}{3} \sin 3pt)$ $t=0 \text{ to } t=\pi/p$ $E_0=1 \frac{\text{volt}}{\text{metre}}$	$p^2=10^7$	
"Innocuous Pulse" of Moullin.		6.5506	$6.5142 \times 10^{-8}$
(7)	$E=E_0 e^{-\frac{1}{2}pt} \sin pt$ $t=0 \text{ to } t=+\infty$ $E_0=1 \frac{\text{volt}}{\text{metre}}$	$p^2=10^7$	
Damped Sine Wave .....		$3.9625 \times 10^6$	$3.9615 \times 10^1$
(11)	$E=E_0 \sin pt$ $t=0 \text{ to } t=800 \pi/p$ $E_0=1 \frac{\text{microvolt}}{\text{metre}}$	$p=2\pi \times 3 \times 10^4$	
C.W. Dot: 400 oscillations.		$\lambda=10 \text{ km.}$ $4.444 \times 10^3$	$1.1487 \times 10^{-6}$
C.W. Dot as above, but with		$\lambda=1 \text{ km.}$ $1.1487 \times 10^{-4}$	$4.4444 \times 10^1$

The Complete Sine Wave  $E=E_0 \sin pt$ ,  $t=0$  to  $t=2\pi/p$  gives figures identical with those of the half-sine wave.

In cases where  $(X_q)^2$  is zero at 10 km. or 1 km. the average value near those wave-lengths is given.

### III. THE RESPONSE OF A RESONANT SYSTEM.

Formulæ have been developed, giving the response  $\left(\int_0^\infty \text{current}^2 \cdot dt\right)$  of receiving systems of given decrement to transmissions with logarithmic decay, by Bjerknes and others, of type

$$\int_0^\infty Q^2 dt \propto \frac{1}{\delta_1 \delta_2} \cdot \frac{\delta_1 + \delta_2}{\left(\frac{\Delta p}{p}\right)^2 + \left(\frac{\delta_1 + \delta_2}{2\pi}\right)^2}.$$

This formula assigns to transmitter and receiver (interchangeable) flatnesses of tuning, of particular shape, and of effective width proportional to the decrement. It has often been asked if similar flatnesses might not be assigned to transmissions with any kind of damping.

This is done by (4)

$$\pi \int_0^\infty Q^2 dt = \int_0^\infty |X_q|^2 \cdot |Y_q|^2 \cdot dq.$$

The interchangeable flatnesses of transmission and reception are  $|X_q|$  and  $|Y_q|$ , and they are in a sense additive. Thus we see that the periodogram gives the flatness of tuning of a transmission in exactly that sense in which the receiver resonance curve gives the flatness of tuning of reception. If the receiver is infinitely selective, there is a flatness of tuning given by the periodogram alone.

Indeed, it may be seen at once that the free vibration (complementary function) of a quiescent LC circuit having no resistance is given for any pulse form in magnitude and phase by the complex  $L^{-1} \left[ \frac{-f(0)}{D + iq_0} \right]$ ,  $(q_0 = \frac{1}{\sqrt{LC}})$ , which is  $X_{q_0}/L$ . The free vibration in the case of all pulses save the infinitely long, centrally tuned sine wave, may be regarded as contributing the whole of  $\int_0^\infty Q^2 dt$  in the case of  $R=0$ .

We have to consider circuits of finite decrement, and also circuits having resonance curves of any shape whatever.

Consider  $|Y_q|^2 (Q, E)$  for an LRC circuit of decrement  $\delta$  (defined as  $\frac{R}{\pi} \sqrt{\frac{C}{L}}$ ), where  $Q$  is the current and  $E$  the induced voltage. Let the pulse be of the type (10)

$$|Y_q|^2 = \frac{q^2 C^2}{(1 - q^2 L C)^2 + q^2 C^2 R^2}$$

and

$$\begin{aligned}\int_0^\infty Q^2 dt &= \frac{1}{\pi} \int_0^\infty |X_q|^2 \cdot |Y_q|^2 \cdot dq \\ &= \frac{I^2}{\pi} \int_0^\infty |Y_q|^2 dq,\end{aligned}$$

integrating

$$\int_0^\infty Q^2 dt = \frac{I^2}{\pi} \cdot \frac{1}{\sqrt{LC}} \cdot \frac{\pi^2}{2\delta}.$$

The current<sup>2</sup> response is therefore finite, and  $\propto \delta^{-1}$ , even though the pulse, acting on a pure resistance, would supply infinite energy.

The current<sup>2</sup> response for a long, centrally-tuned sine wave  $\propto \delta^{-2}$ , so the ratio

$$\frac{\text{received signal energy}}{\text{received static energy}} \propto \delta^{-1}$$

for pulse (8), and it is easy to see that an alteration of  $|X_q|^2$  for values of  $q$  far from  $q_0 \left( = \frac{1}{\sqrt{LC}} \right)$  will be without effect if  $\delta$  is sufficiently small.

For  $\delta \ll 1$ , the result will be true for any atmospheric pulse. By employing a sufficiently low decrement, the signal: static ratio might be made as great as is desired.

It is therefore necessary to discuss the ratio in the case when selectivity is definitely limited, to prevent "ringing" or distortion of signals.

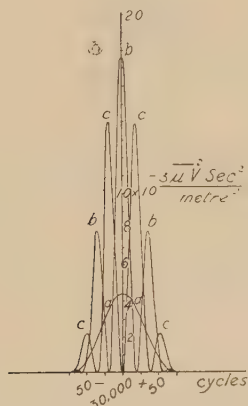
We have no direct knowledge of the initial amplitude and form of the free oscillations, in a system of arbitrary resonance curve; the amount of distortion may, however, be deduced

in a simple way. Consider the response  $\left( \int_0^\infty Q^2 dt \right)$  to a signal consisting of two dots, separated by a space, the second having an arbitrary phase relationship with the first.

If "ringing" is present, the response will be dependent on this phase relationship, but if no such dependence occurs,  $Q$  due to the first dot must necessarily have died out during the space. Periodograms of two spaced dots, syn- and anti-phased, are given in fig. 12, in which it will be noticed that (syn) the peak of  $|X_q|^2$  is raised (4:1) and narrowed, and (anti) the peak splits up into two with a central zero. If (anti) both these peaks fall under the flat top of the  $|Y_q|^2$  peak, the response will be approximately the same as in the syn case. If the  $|Y_q|^2$  peak is as sharp as the principal peak in the syn case, the response will exceed that in the anti-case considerably.

Another aspect of the matter is obtained by comparing two resonance curves which have (a) the same peak height—and therefore receive long dashes equally; (b) the same total area—and therefore give equal responses to pulses of type (10). The best will be that which gives the greatest response to an isolated dot.

Fig. 12.



$|X_q|^2$  as a function of  $\nu = \frac{q}{2\pi}$  in the neighbourhood of  $\nu = 30,000$  (10 km.).

- a. Periodogram of one C.W. Dot.
- b. " two synphased C.W. Dots.
- c. " two antiphased C.W. Dots.

Wave-length of transmissions 10,000 metres.

Number of oscillations in one dot 400.

( $m=400$ , 95 words per minute.)

Maximum field-strength at receptions  $10 \mu\text{V}/\text{metre}$ .

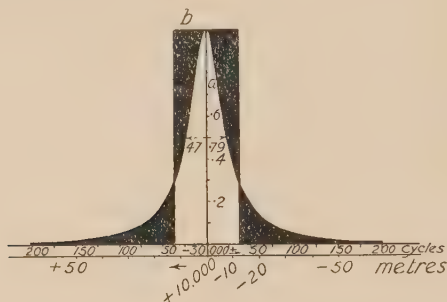
Clearly a pointed peak and a rounded foot are bad features, and though the nature of the argument is such as to preclude an absolutely final decision, the optimum shape would appear to be  $|Y_q|$  zero except over a range  $q_0 \pm \Delta_q$ , where  $\Delta_q$  is dependent on the allowable distortion. A particular case is shown in fig. 13 where a simple LRC resonance curve is shown of  $\delta = .005$ , and also a square-topped, vertical-sided curve of equal height and area.

We have considered a transmitter in which the aerial current assumes its steady-state value at the instant the key is depressed. In high-speed signalling without spacing waves, it may be necessary to take account of the slow building up of the oscillations. This may be done by plotting periodograms from the oscillograms of dots, by the



envelope formula, or by superposing the antenna resonance curve on that of the receiver, though the latter method is approximate only, in view of non-linearity in the behaviour of triode and other generators.

Fig. 13.



(Width (square-topped) = width of  $|Y_q|^2$ , (LRC circuit), at half height)  $\times \frac{\pi}{2}$ .

The periodogram of two anti-dots having 400 oscillations is shown (fig. 12). It will be seen that the distortion is considerably less with the square-topped curve.

### *Reception of a Repeated Pulse.*

It has been shown in II. that the energy of a transmission such as the "running dots" of a wheatstone transmitter, or the successive trains of a musical spark set, is concentrated in narrow bands round the harmonics of the note-pulsatance. Such a transmission may be said to be distorted on reception when the principal contribution to the response arises from a peak of the  $|Y_q|^2$  curve of width comparable with the note-pulsatance.

At this point spark-signals give a scratchy sound in telephones, for the response then shows marked dependence on the note-pulsatance—that is, on the (erratic) phase relationship between successive sparks. The position of the harmonic ordinates is shown in fig. 9 for the case of syn- and anti-phased dots, the spaces being equal to the dots in duration.

Unless the permissible distortion is very great, the receiver resonance curve must be approximately as broad as the principal peak of the periodogram of one dot; again, a pointed peak and a rounded foot are bad features as far as the signal : static ratio is concerned.

*Heterodyne Detection and Note Filtration.*

By employing a sufficiently powerful heterodyne of pulsation  $N$ , the detector output due to a sustained signal  $A \cos q_0 t$  may be made as nearly as is desired,

$$KA \cos (q_0 + N)t + KA \cos (q_0 - N)t,$$

where  $K$  is a constant depending on the detector and the heterodyne strength. Imagine the pulse  $E=f(t)$  analysed as a Fourier series over a very long period  $T$ . If this period is made sufficiently long, the detector output,  $Q$ , due to the pulse, computed as the sum of the outputs due to each term of the series will be independent of small variations of  $T$ . We may therefore suppose that  $T$  contains an integral number of heterodyne oscillations.

All the terms in the output,  $Q$ , will therefore be harmonic with respect to  $T$ , and  $\int_0^\infty Q^2 dt$  will be given by the sum of the contributions which each harmonic would make, in the absence of the rest.

Any one term in the output arises from two terms in the detector input. Suppose that the note selection following detection is such that only a particular band of pulsataces,  $q_a$  to  $q_b$ , in the detector output need to be considered. This band will arise from two bands  $(q_a + N)$  to  $(q_b + N)$  and  $(q_a - N)$  to  $(q_b - N)$  in the detector input.

If the selection preceding detection is such that only one of these bands need be considered, the terms lying within this band contribute independently to the detector output.

Then  $\int_0^\infty Q^2 dt$  may be computed by incorporating the high- and low-frequency selectivities into one resonance curve

where  $\frac{\text{Output—mean square}}{\text{Input—mean square}}$  is plotted for various values of  $q$ .

If, therefore, we possess filter circuits which pass appreciably only pulsataces lying within a given band, we can in effect narrow that band by heterodyning before performing the final selection. It is, however, necessary to precede heterodyning by selection so good that a given note pulsatace can arise appreciably from one H.F. pulsatace only.

We have assumed that resonant systems can be realized which have peaks with sensibly vertical sides and flat tops. Cascaded selections in circuits with moderate decrement (Campbell filters) produce a resonance curve approximating

more closely to this ideal than does one selection in a circuit of very low decrement; if the decrements are so chosen that the curves cross at particular values of  $q$ , and the curves are so scaled that the peak heights are identical, the cascaded-selection curve between these points is never lower, and outside them is never higher than the single-selection curve.

Circuits will readily suggest themselves in which  $|Y_q|^2$  may be made proportional to any powers of  $q$  and  $q^{-1}$ , as  $q$  approaches zero and infinity. It should be noted that in computing  $|Y_q|^2$  for  $q$  large, the increase in H.F. resistance due to skin effect, distributed capacity and radiation should be taken into account.

Triode assemblies in which the amplification is linear, and the retroaction insufficient to produce sustained oscillations, have the property that every possible free vibration has a finite, positive, damping exponent; the method is therefore applicable to non-oscillatory amplifiers, and the desirable cascading of selections, each of moderate decrement, may well take place in such amplifiers. It is a matter of complete indifference at what point in the system Antenna-Detector circuit the lowest decrement is placed. Two cases call for special attention: the so-called aperiodic antenna, and the closed coil aerial.

#### *The Aperiodic Antenna.*

An antenna of capacity  $C$  is earthed through a resistance  $R$ . The grid-filament of a triode is connected across  $R$ . We examine the grid voltage due to  $E$ ,

$$|Y_q|^2 = 1 - \frac{1}{1 + q^2 C^2 R^2},$$

and is thus constant for  $q$  large, and tends to zero as  $q$  approaches zero. The signal: static ratio is therefore best, not when  $R$  is very large, but at some point such that  $|Y_q|^2$  is appreciably less than 1. (See fig. 14.) The contribution

to  $\int_0^\infty Q^2 dt$  from higher values of  $q$  than  $q_0$  is not appreciably altered; that from the lower values of  $q$  is lessened considerably.

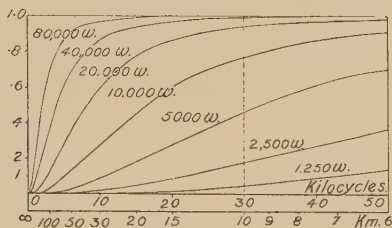
#### *The Closed Coil Aerial.*

The pulse  $E = f(t)$  acts in opposing senses on each limb, with a time lag of  $t = -r/c$ , where  $r$  is the distance between the limbs and  $c$  is the velocity of light, and the plane of the

coil is perpendicular to the wave front. Then  $|X_q|$  for the line-integral of electric force round the frame is thus obtained by multiplying  $|X_q|$  of  $f(t)$  by  $2 \sin qr/2c$ .

Thus  $\int_0^\infty Q^2 dt$  for the open antenna is  $\int_0^\infty |X_q|^2 \cdot |Y_q|^2 \cdot dq$ , while for the closed coil it is  $4 \int_0^\infty |X_q|^2 \cdot |Y_q|^2 \cdot \sin^2 qr/2c \cdot dq$ .

Fig. 14.



$$|Y_q|^2 = \frac{1}{1 + q^2 C^2 R^2} \quad C = 1 \mu\text{F.}$$

Family of Curves for different R.

The frame is therefore fundamentally different from the open antenna in that the contribution to  $\int_0^\infty Q^2 dt$  from values of  $q < \pi c/r$  is reduced. But if the decrement is sufficiently low, the only part of the contribution that need be considered is that arising from a band of width proportional to the decrement, centred round  $q = q_0$  (signal pulsance) over which the factor  $\sin^2 qr/2c$  is approximately constant, and affects the signal and static responses equally.

Thus, apart from directivity, the low decrement frame gives approximately the same signal : static ratio as an open antenna of equal decrement. In the same way, the aperiodic antenna, if followed by a circuit of sufficiently low decrement, confers no appreciable advantage. It is only when the selectivity of the later stages is limited that there is a gain.

In the systems considered, though the shape of the resonance curve has been imagined entirely at our disposal, the ratio

$$\frac{\int_0^\infty Q^2 dt (\text{signal})}{\int_0^\infty Q^2 dt (\text{static})}$$

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can only approach the ratio

$$\frac{|X_q|^2(\text{signal})}{|X_q|^2(\text{static})},$$

and can never exceed it.

### *On the Limiter-Selector Method.*

In closing our brief survey of atmospheric elimination by linear selective methods, let us note one numerical example of the pitfalls awaiting those who would exceed the "ideal" signal: stray ratio by the employment of receivers having a limiting action.

Consider pulse (3)

$$E = E_0 \alpha t e^{-\alpha t} \quad \text{for } t=0 \text{ to } t=\infty, \quad |X_q|^2 = \frac{\alpha^2 E_0^2}{(\alpha^2 + q^2)^2}.$$

Let this pulse act (a) on a circuit of decrement  $\delta$ , where  $\delta \ll 1$ , tuned to  $q_0$ ; (b) on a limiting device with a sharp or slightly rounded cut-off, after which the limited pulse acts on the low decrement circuit of (a).

In the case (b), if limiting occurs at  $t_1$ , where  $\alpha t_1 \ll 1$ , the pulse may be considered as approximately  $E = E_0 \alpha t$  from  $t=0$  to  $t=t_1$ , and  $E_0 \alpha t_1$  until limiting ceases, and from that time till  $t=\infty$ ,  $E = E_0 \alpha t e^{-\alpha t}$ . We will suppose  $t_1$  to be several signal periods,  $2\pi/q_0$ .

The discontinuities introduced by limiting occur at an interval having no special relation to  $2\pi/q_0$ , the signal period. Therefore in computing  $|X_{q_0}|^2$  according to the method outlined for the general type, we must compute  $|X_{q_0}|^2$  for each discontinuity separately, and add the values so obtained. A lower limit to  $|X_{q_0}|^2$  (limited) is obtained by considering only the first two discontinuities, in which the jumps of  $dE/dt$  are  $+\alpha$  and  $-\alpha$ . Then  $|X_{q_0}|^2$  (limited) is  $2\alpha^2 E_0^2 / q_0^4$ , which exceeds slightly  $2|X_{q_0}|^2$  (unlimited), (in practice,  $\alpha \ll q_0$ ).

Further, if the limiter has a slightly rounded cut-off, provided the rounding of the discontinuity in  $dE/dt$  at  $t_1$  is complete in an interval not greater than a half period of the signal ( $\pi/q_0$ ), the effect on  $|X_{q_0}|^2$  is small.

The act of limiting, then, has doubled  $|X_{q_0}|^2$  and has therefore doubled  $\int_0^\infty Q^2 dt$  in the low decrement circuit, and it may be seen that in the case of a pulse containing, when unlimited, only discontinuities in the higher derivatives,  $|X_{q_0}|^2$  may be increased in an even greater ratio.



Though we have examined only one particular case, it is enough to show that considerable analysis is necessary before we can say with L. B. Turner \* that, granted a suitable limiter, the limiter-selector method provides, even in theory, a solution of the atmospheric problem.

#### IV. CONCLUSION.

Means have been given for plotting the density of amplitude and square of amplitude of a non-periodic pulse over the wireless spectrum.

The response created in a resonant system of entirely arbitrary resonance curve has been examined, in terms of the periodogram of the pulse, or resonance curve of contained frequencies, and it has been shown that only a finite range of frequencies in the wireless spectrum are of practical importance.

The best form of resonance curve for the reception of morse signals and the elimination of interference has been shown to have vertical sides and a flat top; this implies a multiplicity of selecting circuits, the order of which is unimportant.

The benefit accruing from the use of the aperiodic antenna, and the loop antenna (apart from directivity) has been shown to be small. The paper demonstrates the existence of a maximum signal : stray ratio which can never be exceeded, with linear apparatus, and indicates a possible weakness of limiting systems.

In conclusion, we have pleasure in expressing our thanks to Professors B. van der Pol, W. H. Eccles, G. I. Taylor, C. L. Fortescue, and especially to Dr. A. Koerts, for their kind interest and criticisms, and to Mr. A. P. M. Fleming, C.B.E., M.I.E.E., M.Sc Tech., Director of Research, Metropolitan-Vickers Electrical Company Limited, for his kind permission to publish this investigation.

Research Laboratories,  
Metropolitan-Vickers Electrical Co. Ltd.,  
Trafford Park, Manchester.

\* L. B. Turner, 'Outline of Wireless.'



LII. *A Proposed Test of the Space Quantization of Atoms in a Magnetic Field.* By ARTHUR EDWARD RUARK and G. BREIT \*.

§ 1. **T**HE experiment of Stern and Gerlach † shows that the space quantization of atoms is obeyed by the atoms of many elements. The technical difficulties of this experiment are so great that it is desirable to devise other means of testing the space quantization.

Further, the results of the Stern and Gerlach experiment yield only the component of the magnetic moment of the atom parallel to the field. This leaves a gap in our knowledge which is very undesirable for reasons which are well illustrated by considering Bohr's model of the helium atom. This model is paramagnetic, while helium gas is diamagnetic. To explain this, Bohr assumes the space quantization of normal helium to be such that all the atoms place themselves with their axes of angular momentum perpendicular to the field. There is thus no positive contribution to the susceptibility, and the gas is diamagnetic. If the Stern and Gerlach experiment for helium, assuming it possible, were to show that helium atoms are undeflected, it would not decide between the view of Bohr outlined above, and the view that the helium atom has no magnetic moment, and can take up any orientation whatever with respect to the field.

The fundamental question to be decided is whether properties of matter in bulk may be used. If such is the case the unidirectional stream of atoms may be dispensed with and the test for the space quantization can be conducted by means of any property of matter which has a vector character and which depends on the state of atoms in their normal energy level. Thus, if all atoms, say of helium, should be orientated with their axes of angular momentum perpendicular to the direction of the magnetic field, then we should expect helium to have a different dielectric constant depending upon whether the applied electric field is perpendicular or parallel

\* Communicated by the Authors. Published by permission of the Director of the Bureau of Standards, Department of Commerce, and of the Director of the Department of Terrestrial Magnetism, Carnegie Institution of Washington.

† See Gerlach and Stern, *Ann. d. Phys.* lxxiv. p. 673 (1924), for bibliography.

Gerlach and Cilliers, *ZS. für Phys.* xxvi. p. 106 (1924).

to the applied magnetic field. Similarly the thermal conductivity or the viscosity might be supposed to be different, according as to whether the temperature or velocity gradient is perpendicular or parallel to the applied field.

Of course, if the atoms were orientated at random, the vector properties of the gas would be slightly different in directions parallel and perpendicular to the field, because of the Larmor precession. But the ratio of the change in any quantity measured first along and then across the field to the quantity itself is negligibly small in all cases of practical interest. Here we are speaking of effects due to the pseudo-crystalline state of the gas, caused by space quantization.

It may be possible to construct theories which will predict differences in the magnitude of such quantities as the dielectric constant, the refractive index, or the magnetic rotation of the plane of polarization, according as we adopt the hypothesis of space quantization or that of random orientation. However, it seems preferable to consider only the change of properties with direction in the magnetic field, since we are then independent of questionable theories.

§ 2. We must decide, therefore, whether it is rational for the consequences of space quantization to be applied to properties of matter in bulk. In the case of some properties the probability of an anisotropic nature with respect to the field seems very questionable. Thus in discussions of viscosity, the mean free path in various directions is the determining factor. When atoms collide the interactions may be supposed to be of such a radical character as to make the presence of the external magnetic field of no consequence. Similarly with thermal conductivity.

The case is different with such a property as the dielectric constant. The time which an atom spends between collisions is large compared with the time occupied by a collision, and the only essential condition therefore is that the space quantization should predominate over a random orientation during an appreciable portion of the time between two collisions.

Little information is available as to the time necessary for space quantization to set in. No evidence of lag was found in the experiment of Stern and Gerlach. Their test for the presence of undeflected atoms is very delicate, and in the case of silver all atoms are deflected. The difficulties of understanding the rapidity of orientation have been brought

out by Einstein and Ehrenfest \*. The other and less direct line of evidence comes from data on paramagnetism which appear to be in satisfactory agreement with the theory of space quantization, using the Bohr magneton as the quantum of magnetic moment †.

If the Bohr magneton may be used in Pauli's manner for a material in bulk, then it is rational to expect space quantization to be applicable and it appears safe to say that orientation takes place in a small fraction of the time between collisions.

Such a state of affairs would occur in oxygen gas and NO. Similarly, paramagnetic salts must satisfy the space quantization conditions.

The evidence concerning the Bohr magneton may be criticised, however, as is done by Weiss ‡ from the purely experimental point of view, and also because the data of Wood and Ellett § on the polarization of resonance radiation seem to indicate that the time which is necessary for the establishment of space quantization in an excited state is of the same order of magnitude as the period of the Larmor precession in the magnetic field applied.

For weak fields the period of the Larmor precession is likely to be longer than the mean time between collisions. However, with fields of the order of 10,000 gauss the Larmor precession has a period of the order of  $6 \cdot 10^{-11}$  sec., which is smaller than the mean time between collisions of say helium, at atmospheric pressure ( $\cong 3 \times 10^{-10}$  sec.). We see therefore that with fields of reasonable strength, we can expect an anisotropic effect on the dielectric constant.

§ 3. We must discuss next the feasibility of obtaining anisotropic electric effects by the action of the magnetic field from the point of view of the reciprocity of action of these two fields. We can make use in this of the very lucid treatment of Klein || of the perturbations in the motion of an electron in a hydrogenic orbit under the simultaneous action of an electric and a magnetic field. The results of this treatment are these. Let us denote the electric and magnetic

\* *ZS. für Phys.* xi. p. 31 (1922).

† W. W. Pauli, Jr., *Phys. Zeit.* xxi. p. 615 (1920). Epstein, *Science*, lvii. p. 532 (1923). Sommerfeld, *ZS. für Phys.* xix. p. 221 (1923). Dorfmann, *ZS. für Phys.* xvii. p. 98 (1923). Weiss, *Journal de Phys.* iv, p. 153 (1923), and v. p. 129 (1924).

‡ *Journal de Phys.* v. p. 129 (1924).

§ *Proc. Roy. Soc., A*, ciii. p. 396 (1923).

|| Oskar Klein, *ZS. für Phys.* xxii. p. 109 (1924).

intensities by  $\mathbf{E}$  and  $\mathbf{H}$  respectively, and let

$$\left. \begin{aligned} \mathbf{A} &= \frac{e}{2mc} \mathbf{H} + ek \mathbf{E}, \\ \mathbf{B} &= \frac{e}{2mc} \mathbf{H} - ek \mathbf{E}, \\ k &= \frac{3}{4\pi ma\omega}. \end{aligned} \right\} \dots \dots (3)$$

Here  $e$  and  $m$  are the charge and mass of the electron;  $2a$  is the major axis of the undisturbed orbit and  $\omega$  the frequency of revolution of the electron, while  $c$  is the velocity of light. Defining two vectors

$$2\mathbf{U} = \mathbf{R} + k\mathbf{P},$$

$$2\mathbf{V} = \mathbf{R} - k\mathbf{P},$$

where  $\mathbf{R}$  is the vector drawn from the nucleus to the electrical centre of the osculating orbit and where  $\mathbf{P}$  is the angular momentum of the osculating orbit, the following relations hold :

$$\frac{d\mathbf{U}}{dt} = [\mathbf{A}, \mathbf{U}]$$

$$\frac{d\mathbf{V}}{dt} = [\mathbf{B}, \mathbf{V}].$$

These equations express the fact that the vectors  $\mathbf{U}$ ,  $\mathbf{V}$ , rotate with the angular velocities  $\mathbf{A}$ ,  $\mathbf{B}$ , respectively.

If  $\mathbf{E}$  is sufficiently small compared with  $\mathbf{H}$ ,  $\mathbf{A} \cong \mathbf{B}$  and the whole orbit may be thought of as precessing with the angular velocity  $\frac{e}{2mc} \mathbf{H}$ . Since we are concerned with quantization

under these conditions, it is convenient for us to choose  $\omega t$ ,  $At$ , and  $(A-B)t$  as the angular variables of the system. Calling these  $w_1$ ,  $w_2$ , and  $w_3$  respectively, the momentum associated with  $(A-B)t$  is to satisfy the relation  $J_3 = n_3 h$ . If  $A \rightarrow B$  the period corresponding to  $w_3$  may become long in comparison with the mean time  $\tau$  which the atom is likely to spend in an excited state [approximately the time constant of a radiating electron]. If such is the case, the quantization associated with  $J_3$  is likely to be ineffective (by analogy with the case of the experiments of Wood and Ellett). Fields smaller than 1 volt/cm. make the time  $> 2 \times 10^{-7}$  sec., and thus one may hope to obtain the effect of an electric field by considering the quantum states determined by the magnetic

field and the small distortions in these states due to the electric field\*.

Further, regardless of the magnitude of  $\tau$ , if the period of  $\omega_3$  is long in comparison with the period of  $\omega_2$  we deal with a small Stark effect and a large Zeeman effect, and it is clear that each of the Zeeman components is subdivided into a number of Stark components. These correspond to different values of  $J_3$  and to the same value of  $J_2$ . On account of the vector character of the expressions for  $\mathbf{A}$  and  $\mathbf{B}$  in terms of  $\mathbf{E}$  and  $\mathbf{H}$  there is in general an anisotropic property of each Zeeman term with respect to its Stark components depending upon whether the fields  $\mathbf{E}$ ,  $\mathbf{H}$  are parallel or perpendicular to each other. Thus, *e. g.*, if  $\mathbf{E}$  and  $\mathbf{H}$  are perpendicular to each other,  $\mathbf{A}$  and  $\mathbf{B}$  are equal to each other in absolute value for small  $\mathbf{E}$  so that the influence of  $\omega_3$  is negligible, while if  $\mathbf{E}$  and  $\mathbf{H}$  are parallel this is not the case. The quantum nature of the Stark effect becomes apparent therefore in the longitudinal arrangement of fields before it is felt in the transverse position.

A difference in the dielectric constant in two directions implies double refraction for long waves. Double refraction for radiation in general is caused by the presence of the magnetic field. In how far this refraction is a direct function of the orientation of the atom in the lowest energy state is difficult to say: the characteristics of higher states may also be involved. In the neighbourhood of absorption frequencies the effect merges with the Zeeman effect.

An experimental test of the ideas in § 1 and § 2 seems readily possible. The method of heterogeneous beats should be capable of revealing variations in the dielectric constant of helium with direction in the magnetic field.

(A. E. R.) Bureau of Standards,  
(G. B.) Dept. of Terrestrial Magnetism,  
Washington, D.C.,  
September 27, 1924.

\* Since in this case there are only two angular variables and three coordinates the system is degenerate unless relativistic mechanics are used. The question as to what happens to the character of the relativistic system in the presence of an electric field simultaneously with the magnetic is not clear.



LIII. *On the Frequency of the Eddies generated by the Motion of Circular Cylinders through a Fluid.* By E. F. RELF, A.R.C.Sc., and L. F. G. SIMMONS, B.A., A.R.C.Sc.,\* of the Aerodynamics Department, National Physical Laboratory.

**I**N a previous communication † a comparison was made between the frequency of the eddies generated behind a circular cylinder, (i.) as observed directly in a water channel and (ii.) as deduced from the singing of fine wires exposed to a current of air. It was shown that the frequency of the note heard in the second case agreed with the frequency of the eddies formed in the first case, provided that the comparison was made under conditions which were identical according to dimensional theory,—i. e., at the same value of the “Reynolds’ number”  $VD/\nu$  ‡.

The present paper describes measurements of the eddy frequency conducted at higher values of  $VD/\nu$  ‡. These reveal an interesting connexion between frequency and the drag coefficient, which is clearly shown by the accompanying diagram.

The frequencies measured were in general too low to permit aural determination, and a new method had to be employed. Cylinders of various diameters were placed in a wind-tunnel, extending from wall to wall, and a short platinum wire about 0.001 in. diameter was mounted parallel to the axis of the cylinder, usually about two diameters downstream. The wire was heated by means of an electric current until it was on the point of glowing. In order to measure the frequency of the current charges induced by the eddy motion, a step-up transformer was included in the heating circuit, the secondary of which was connected through suitable resistances to a vibration galvanometer. At each wind speed, the tuning of the galvanometer was adjusted until marked resonance occurred. Under these conditions the natural frequency of the galvanometer coincided with that of the disturbance; the galvanometer was then connected to a single phase alternator, and the speed of rotation of the alternator varied until resonance was again obtained, when an observation of the alternator speed led at once to a determination of the frequency to which the galvanometer had been tuned. The process was repeated at

\* Communicated by Mr. R. V. Southwell.

† Relf, *Phil. Mag.* ser. 6, xlii. p. 173 (1921).

‡  $V$  here denotes the free-stream velocity,  $D$  the diameter of the cylinder, and  $\nu$  the kinematic viscosity.



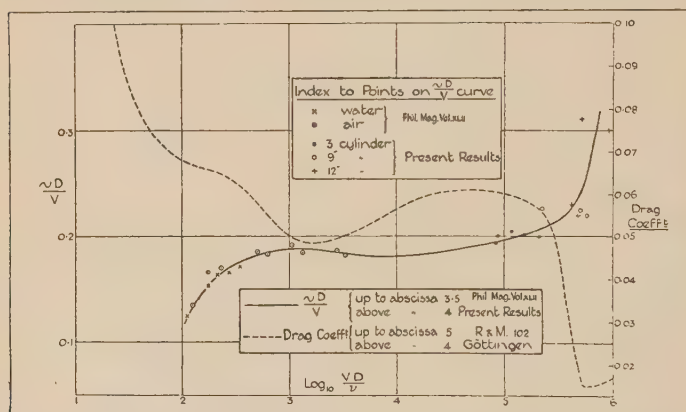
# 510 *Eddies generated by Circular Cylinders through a Fluid.*

various wind speeds between 20 and 60 ft./sec. with cylinders of 3 in., 9 in., and 1 ft. diameter.

The results obtained from the experiments are shown in the figure, together with corresponding results from the earlier paper cited above, and a curve of drag coefficient\*.

The ordinates of the full-line curve represent values of  $\frac{\sim D}{V}$  plotted against  $\log_{10} \frac{VD}{\nu}$ , where  $\sim$  is the eddy frequency.

It will be seen that there is a definite relationship between the curves of frequency and resistance, inasmuch as a reduction in drag coefficient corresponds with a rise in the eddy frequency. This is especially marked in the regions comprised between  $\log_{10} VD/\nu=2$  to 3, and 5 to 6. Below



$VD/\nu=100$  eddy motion does not occur, and in this region it has been shown that† the drag coefficient is calculable with reasonable accuracy from Oseen's approximation to the equations of motion. Between  $VD/\nu=100$  and 1000 the drag coefficient falls, reaching a minimum at about  $VD/\nu=1600$ , while the eddy frequency rises to a maximum at about the same value of  $VD/\nu$ .

The special interest of the present results is in connexion with the rapid fall of drag coefficient in the region between  $VD/\nu=10^5$  and  $10^6$ , which was first observed in experiments at Göttingen‡ and later confirmed by tests made at the

\* The curve of drag coefficient has been taken from tests on the resistance of wires, made at the N. P. L. (Advisory Committee for Aeronautics, R. and M. 102) up to  $VD/\nu=10^4$ , and from experiments made at Göttingen (*Phys. Zeits.* 1921, p. 332) for higher values of  $VD/\nu$ .

† Bairstow, Cave, and Lang, *Proc. Roy. Soc. A. c.* pp. 394-413 (1922).

‡ *Loc. cit.*

National Physical Laboratory. Measurement of eddy frequency in this region was very difficult, as would be expected from the obviously critical nature of the flow, and no definite periodicity at a given wind speed could be observed. It was, however, possible in all cases to measure the frequencies of the most prominent disturbances present: these figures are plotted in the curve, and there can be no doubt that the frequency rises rapidly at the value of  $VD/\nu$  where the rapid fall in drag occurs. The precise nature of the change of flow occurring in this region cannot be determined by experiments of the kind here described, and observations by means of smoke would be very difficult, if not impossible, owing to the high wind speed necessary with a cylinder of reasonable diameter. It is considered probable that the general eddy motion filling the whole space behind the cylinder (which has often been observed photographically at lower values of  $VD/\nu$ ) is giving place to a dead-air region which is fringed by smaller eddies. This explanation, though it can at present only be regarded as tentative, seems to account for the rise of eddy frequency observed, and also for the rapid fall of drag coefficient.

So far as the writers were able to determine with the means at their disposal, the flow at values of  $VD/\nu < 10^3$  was accurately periodic, whilst above this limit (*i. e.* in the critical region) the flow was definitely aperiodic.

LIV. *On Strain Components in Curvilinear Coordinates.* By A. W. CONWAY, M.A., D.Sc., F.R.S., University College, Dublin\*.

THE following method of obtaining the strain components is, perhaps, less difficult than those usually given in treatises on elasticity. Let the square of the line element  $ds^2$  in any system of orthogonal coordinates be given by

$$ds^2 = g_1 dx_1^2 + g_2 dx_2^2 + g_3 dx_3^2.$$

Let the infinitesimal displacements be determined by the changes  $\phi_1, \phi_2, \phi_3$  in the coordinates  $x_1, x_2, x_3$ . The actual displacements  $(u_1, u_2, u_3) = (\sqrt{g_1}\phi_1, \sqrt{g_2}\phi_2, \sqrt{g_3}\phi_3)$  and the direction cosines

$$(l_1, l_2, l_3) = (\sqrt{g_1} dx_1/ds, \sqrt{g_2} dx_2/ds, \sqrt{g_3} dx_3/ds).$$

Let  $(l_1, l_2, l_3)$  be the direction cosines of a straight line  $P_0P_1$  of any length. Let  $P_0', P_1'$  be the extremities of the

\* Communicated by the Author.

deformed line and  $P_0'', P_1''$  the projections of  $P_0', P_1'$  on  $P_0 P_1$ . Then for an infinitesimal displacement the increase of length of  $P_0 P_1$  is  $P_0'' P_1'' - P_0' P_1'$  or  $P_1 P_1'' - P_0 P_0''$ , i. e. the difference between the projections along  $P_0 P_1$  of the displacements of  $P_0 P_1$  or

$$\left[ g_1 \phi_1 \frac{dx_1}{ds} + g_2 \phi_2 \frac{dx_2}{ds} + g_3 \phi_3 \frac{dx_3}{ds} \right]_0^1.$$

Hence if  $P_0 P_1$  is a line element we get for the elongation along  $P_0 P_1$

$$\frac{d}{ds} \sum \left( g_r \phi_r \frac{dx_r}{ds} \right) \quad (r=1, 2, 3).$$

Here we can shorten the expressions by introducing the "dummy" notation of tensor algebra. We have then

$$\begin{aligned} \frac{d}{ds} \left( g_r \phi_r \frac{dx_r}{ds} \right) &= \phi_r \frac{d}{ds} \left( g_r \frac{dx_r}{ds} \right) + g_r \frac{dx_r}{ds} \frac{d\phi_r}{ds} \\ &= \phi_r \frac{d}{ds} \left( g_r \frac{dx_r}{ds} \right) + g_r \frac{dx_r}{ds} \frac{dx_i}{ds} \frac{\partial \phi_r}{\partial x_i}. \end{aligned}$$

The first expression can be transformed by means of the differential equations of a straight line in the coordinates  $x_1, x_2, x_3$ . These of course can be obtained from the equation  $\delta \int ds = 0$  or from the dynamical analogue as follows.

Let a particle of unit mass move along  $P_0 P_1$  with uniform unit velocity, then  $dt = ds$  and the kinetic energy is

$$\frac{1}{2} g_r \left( \frac{dx_r}{ds} \right)^2.$$

Expressing by Lagrange's method that the generalized forces are zero, we get

$$\frac{d}{ds} \left( g_1 \frac{dx_1}{ds} \right) = \frac{1}{2} \left( \frac{dx_i}{ds} \right)^2 \frac{\partial g_i}{\partial x_1}$$

and two similar equations. Inserting in the above relation we get finally for the elongation

$$g_r \frac{dx_r}{ds} \frac{dx_i}{ds} \frac{\partial \phi_r}{\partial x_i} + \frac{1}{2} \phi_r \frac{\partial g_i}{\partial x_r} \left( \frac{\partial x_i}{\partial s} \right)^2.$$

Inserting the values of  $(l_1, l_2, l_3)$  and  $(u_1, u_2, u_3)$  we then obtain the usual expressions. It is of course obvious that the method applies exactly in a similar way to non-orthogonal coordinates.

LV. "Semi-optical" Lines in the X-ray Spectra.  
By E. BÄCKLIN, M. SIEGBAHN, and R. THORÆUS\*.

THE nowadays existing detailed systematization of the X-ray spectra is based upon the assumptions of Kossel, that the X-ray lines are emitted on transitions of electrons between orbits which are normally occupied by electrons. In reality it has been supposed that a certain spectral line disappears at the same time as the electronic shell from which the electron starts, and in general the experiments seem to support this view. Thus we are able to define the true X-ray spectral lines as transitions between energy levels which are normally occupied by electrons. Complementary to this the optical spectral lines belong to transitions from a free outer orbit to a vacant place in the outmost energy shell.

In connexion with some investigations made by Thoræus and Siegbahn† to extend the range of registered wavelengths within the K-series and some peculiarities found by Mr. Bäcklin in the  $K\beta_1$  line of the elements Mg (12) and Na (11), we have performed a particular investigation in order to clear up this point.

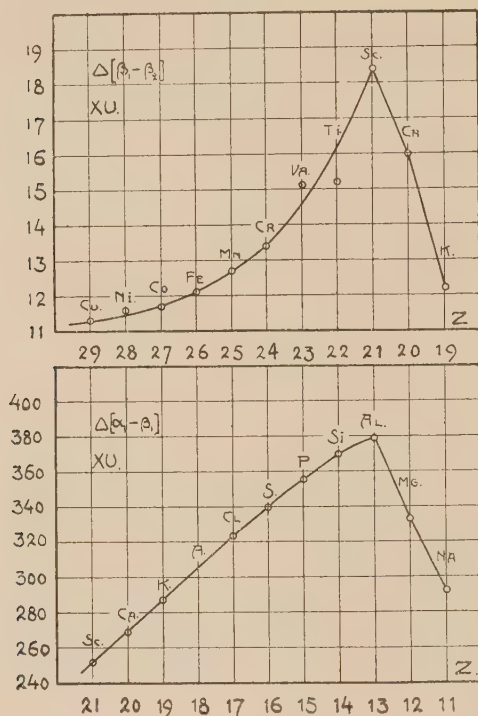
In the investigation mentioned above the K-series of F (9) has been studied. Although the  $K\alpha$  line ( $\lambda = 18.37 \text{ \AA.U.}$ ) was very strong, no trace of the  $K\beta_1$  line was to be seen on the photographic plate. This is quite in agreement with the above criterion on X-ray lines, as the  $K\beta_1$  line belongs to a transition from an M-orbit to the K-shell. At F (9), however, the M-shell is unoccupied, and so the  $K\beta_1$  line cannot be expected. There is no doubt that Na (11) is the last element where the M-level is normally occupied by at least one electron. From Na (11) upwards the  $K\beta_1$  line has been registered and measured, but it may be mentioned that this line is relatively very weak at Na (11), at least in comparison with that one of Al (13). When plotting the wave-length difference  $K\alpha - K\beta_1$  against the atomic number  $Z$  as in fig. 1 b, we get a curve of surprising appearance. The peculiarity of this curve is surely due to the  $K\beta_1$  line and

\* Communicated by the Authors.

† Read before the Royal Swedish Academy of Science, Nov. 26th, 1924, and will appear in *Arkiv f. Mat., Astr. o. Fys.*

514 Messrs. E. Bäcklin, M. Siegbahn, and R. Thorsæus on  
shows that this line behaves quite regularly down to Al (13)  
but is singular at Mg (12) and Na (11).

Fig. 1 *a, b.*



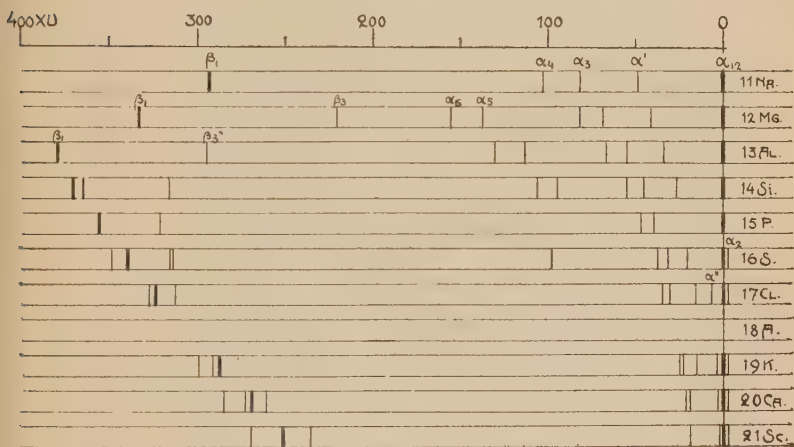
The same phenomenon may also be seen directly on the scheme (fig. 2) of all the K-lines of the elements Na (11) to Sc (21). Here the spectra are arranged one above the other in such a way that the  $K\alpha$  lines are on the same vertical. All the lines excepting  $\alpha$  and  $\beta_1$  are spark lines, which are very common in this region. The irregular displacement of the  $\beta_1$  line at the last two elements Mg (12) and Na (11) is evidently to be seen.

This peculiarity may be considered in the light of the scheme of the atomic model recently given by Stoner\* compared with the systematization of the X-ray spectra. Fig. 3 gives a diagram of the energy levels at Na (11), where 5 (1K, 3L and 1M) are normally occupied by electrons

\* Phil. Mag. ser. 6, xlviii, No. 286, Oct. 1924.

and constitute the X-ray levels. Beneath them the free orbits as given by the ordinary arc spectrum are drawn. Of the 11 electrons, 2 belong to the K-, 8 to the L- and 1 to the first M-level. Now Stoner has put forward the idea, that the 8 electrons of the L-level are distributed as shown in fig. 3, that means 2 in the  $L_I$ , 2 in the  $L_{II}$ , and 4 in the  $L_{III}$ . The 11th electron is then placed in the  $M_I$ .

Fig. 2.



Consequently the  $\beta_1$  line should not exist as a true X-ray line in the K-spectrum of Na (11). The same should occur at the next element Mg (12), where there are 2 electrons in the  $M_I$ -shell. At first at Al (13) the  $M_{II}$ -shell gets one electron, and from this element upwards the true  $K\beta_1$  line should appear.

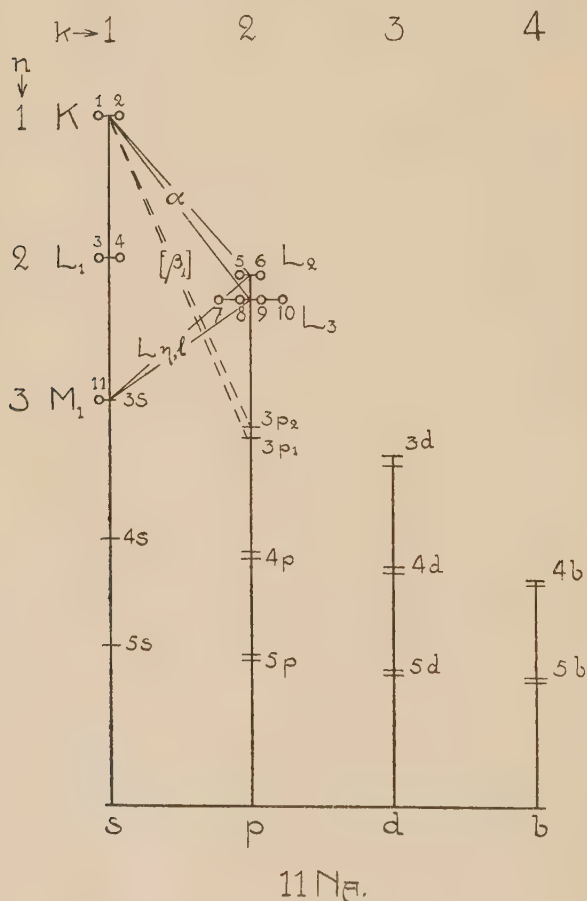
The above is supported by the curve in fig. 1, which shows that the line called  $K\beta_1$  is not a direct continuation of the  $K\beta_1$  of the higher elements. It might be considered as a "semi-optical" line which is emitted by an electron starting from a free level of the atom, or say a true X-ray line belonging to a metastable form of the elements where the outmost electron is moving in another orbit than that one of the normal atom.

Quite the same phenomenon as at Na (11) may also be shown to occur at K (19) where the electronic arrangement is similar to that of Na. But in this case the peculiarity is to be expected in the  $K\beta_2$  line, as may be seen from fig. 4. When plotting the wave-length difference  $K\beta_1 - K\beta_2$  against the atomic number  $Z$  we get a curve fig. 1a, which has the



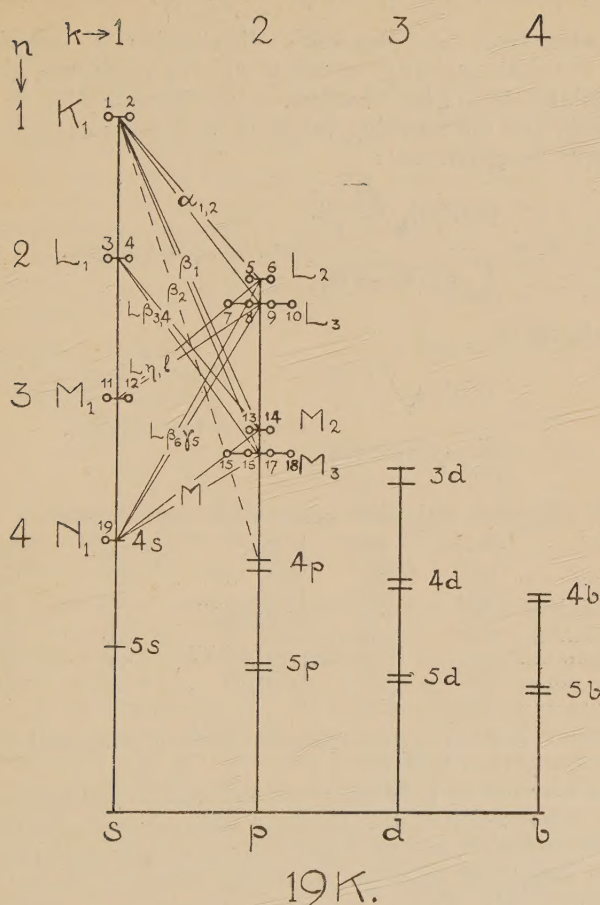
same general appearance down to K (19) as that one of  $K\alpha - K\beta_1$  at the elements next to Na (11). The line called  $\beta_2$  of the two elements Ca (20) and K (19) is displaced against longer wave-lengths.

Fig. 3.



Similar irregularities of the X-ray lines in the neighbourhood of the last element, where the line in question disappears, are also to be found in some other cases. Due to the more complicated structure and building-up process of the higher elements, however, the interpretation is here not as simple as in the two cases discussed above.

Fig. 4.



Upsala, Physical Laboratory.  
Dec. 3rd, 1924.

### LVI. Gas Ion Mobilities.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN an article of mine in your Journal, I derived an expression for ionic mobilities based on a recent theory of J. J. Thomson and a classical equation due to Langevin. In analysing the derivation of Langevin's equation, it appeared that what he calls  $\lambda$  in his equation is  $\frac{1}{\pi\sigma^2N}$ , and not, as has

been supposed, the quantity  $\frac{1}{\pi\sqrt{2}\sigma^2N}$ , containing the correction term for Maxwell's distribution of velocities. Thus the ionic mobility equation which I published, giving the mobility in cm./sec. volt/cm. should be multiplied by  $\sqrt{2}$ , as should also the resulting values of the computed mobility. The equation given was :

$$K = \frac{0.0735 \sqrt{\frac{1+b}{b}}}{\frac{p}{760} \sqrt{(D-1)M_0}} \text{ cm./sec. per volt/cm.}$$

It should be

$$K = \frac{0.104 \sqrt{\frac{1+b}{b}}}{\frac{p}{760} \sqrt{(D-1)M_0}} \text{ cm./sec. per volt/cm.}$$

The computed mobilities in the table then become :—

Gas.	Comp.	Obs.	Gas.	Comp.	Obs.
H <sub>2</sub> .....	6.27	6.02	SO <sub>2</sub> .....	.20	.44
He .....	8.50	5.09	N <sub>2</sub> O .....	.68	.82
A .....	2.32	1.37	C <sub>2</sub> H <sub>5</sub> OH ...	.23	.34
Air .....	1.12	1.35-1.6	CCl <sub>4</sub> .....	.18	.30
NH <sub>3</sub> .....	.41	.74-.52	C <sub>2</sub> H <sub>5</sub> Cl .....	.14	.33
CO <sub>2</sub> .....	.72	.81	C <sub>4</sub> H <sub>10</sub> O .....	.20	.24
CO .....	1.04	1.10			

These, it is seen, in general agree with the observed values more closely than before.

In a footnote on p. 448 a doubt was cast on the legitimacy of the introduction of the Thomson factor into the Langevin mobility equation, and the desirability of a rigorous derivation of the Langevin equation assuming attractive forces was indicated. The writer has since discovered a paper by Langevin in the *Annales de Chimie et de Physique*, viii. 5, p. 238 (1905), in which he makes such a rigorous derivation, starting from a somewhat different viewpoint. The resulting equation for the case of an inverse fifth-power law written in the writer's notation is

$$K = \frac{0.235 \sqrt{\frac{M+m}{m}}}{\sqrt{\frac{p}{760} (D-1) M_0}}.$$

As is seen, this is identical with the writer's equation except for a numerical factor of 0.235 instead of .104, and

except for the fact that it contains  $\sqrt{\frac{p}{760}}$  instead of  $\frac{p}{760}$ ,

The latter difference may be due to a numerical blunder in Langevin's treatment of the constants.

This beautiful piece of analysis therefore completely confirms in its general outlines the conclusions arrived at by the writer, and indicates that in an equation of this type there lies the proper solution of the ionic mobility problem. It is only to be regretted that the lack of experimental development of this field of work at the time of Langevin's paper did not enable him to see its full importance, and thus permit him to give this brilliant piece of work all the publicity it deserved.

Department of Physics,  
University of California,  
Berkeley, California,  
October 11, 1924.

LEONARD B. LOEB.

LVII. *Notices respecting New Books.*

*John William Strutt, Third Baron Rayleigh, O.M., F.R.S.* By his son ROBERT JOHN STRUTT, Fourth Baron Rayleigh, F.R.S. (London : Edward Arnold & Co., 1924.)

IT is a matter of very great satisfaction to Mathematical Physicists, and indeed to scientific men and women generally, to welcome the interesting and vivid account of the great Lord Rayleigh contained in this book. The work of Rayleigh will continue to be of very great importance until the present generation of scientists is long since passed, and the record of his intellectual life and of the activities of his mind are, fortunately, safely preserved for posterity in the 446 papers in the six large volumes of his collected writings. But the memory of Rayleigh as a great figure of a man, would necessarily fade, as those who knew him in turn leave their scientific labours to the next generation. The present Lord Rayleigh, in putting on paper all the many sides of his distinguished father, has earned our gratitude, and we value this record of Rayleigh as a human being, and place it beside his collected works with great satisfaction.

It is unnecessary to give any detailed account of the contents of the book. The varied interests of Rayleigh will make the interesting expositions by the author appeal to almost every scientist, and the account of Rayleigh's every-day life makes an interesting and vivid picture of a great Victorian.

*A History of British Earthquakes.* By CHARLES DAVISON, Sc.D., F.G.S. (Cambridge University Series. 1924.)

By this valuable History and compilation Mr. Davison adds substantially to the services he has already rendered to seismological science. The 'History of British Earthquakes' will save from



oblivion and render available many hundreds of valuable records of earthquakes in Britain.

It is, indeed, an astonishing record. We find no less than 1191 well attested earthquake shocks recorded in the British Isles since the year 974 A.D. Mr. Davison's analysis of these seismic records shows—as might be expected—that repetitional shocks in certain faulted areas account for the greater number of these earthquakes. Thus the Great Glen fault and the Highland Border fault have been specially productive; the latter giving rise to the very large number of closely localized seismic disturbances of the Comrie district. There appears no reason to question the view taken by Mr. Davison that British earthquakes are, in nearly every case, associated with slowly progressing fault-movements. In Mr. Davison's map showing the distribution of British earthquakes we find that the seismic areas are numerous and widely distributed. The author estimates that about half the area of Great Britain has at different historic times been affected by seismic disturbances. He draws attention to the comparative freedom of Ireland from such disturbances.

The question of periodicity is one of great interest, but the analysis of the distribution in time of British earthquakes, although leading to an apparent diurnal periodicity, appears far from decisive. The periodicity may be apparent only, and due—as Mr. Davison suggests—to more favourable conditions for observation recurring at particular times of the day. More definite are conclusions respecting the westerly migration of foci. This phenomenon appears to be frequently exhibited, the stability of the Comrie foci being an interesting exception. Mr. Davison's discussion of twin earthquakes is a good instance of the valuable contributions to seismology which he is able to extract from his great compilation. His already published theory ('Manual of Seismology,' 1921) of the origin of such earthquakes as due to the growth of a crust-fold the axis of which is cut by a fault-plane, appears to be the best explanation so far offered of the occurrence of nearly simultaneous shocks emanating from foci separated by a few miles of inter-focal region.

One lesson of special importance should be learned from these and similar records: the fact of the *constant* yielding of the earth's continental crust to comparatively feeble stresses. We should expect this on *à priori* grounds. For regionally disturbed and faulted rocks will not behave the same as a small hand specimen of flawless rock placed in a hydraulic press. It is sometimes assumed, however, that they will; and upon this assumption a theory of the cyclical development of mountain chains as arising out of an assumed slowly and uniformly cooling and shrinking Earth and the accumulation of strain upon an enormous scale, is based. The seismic phenomena apparent all over the Globe, and emanating from various depths in the crust, demonstrate that such great strains cannot and do not accumulate.

J. J.

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[The Editors do not hold themselves responsible for the views expressed by their correspondents.]